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March 23-26, 1987. Volume 2

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16. ABSTRACT The two-volume proceedings document the 1987 Joint (EPA and EPRI) Symposium on Stationary Combustion NO _x Control, held March 23-26, 1987, in New Orleans, LA. The 49 presentations covered: low-NO _x combustion developments (e.g., reburning and burner design modifications); coal-, oil-, and gas-fired boiler applications; flue gas treatment processes; fundamental combustion studies; and industrial and commercial applications. Also presented were manufacturers' updates of commercially available technology and an overview of environmental issues involving NO _x control. Attendees represented 14 nations. Volume 1 covers Sessions I (background and environmental issues), II (low-NO _x combustion development), III (manufacturers' update of commercially available technology), and IV (coal-fired boiler applications). Volume 2 covers Sessions Va (flue gas treatment), Vb (fundamental combustion studies), VI (cyclone-fired boilers), VIIa (oil- and gas-fired boilers), and VIIb (industrial and commercial applications).		
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PREFACE

The 1987 Joint Symposium on Stationary Combustion NO_x Control was held March 23 - 26, 1987, in New Orleans, Louisiana. This symposium, jointly sponsored by EPRI and EPA, was the fourth of its kind devoted solely to the discussion of control of NO_x emissions from stationary sources. Specific topics discussed included the low-NO_x combustion developments such as reburning and burner design modifications, coal-, oil-, and gas-fired boilers applications, flue gas treatment processes, fundamental combustion studies, and industrial and commercial applications. Also presented were manufacturers' updates of commercially available technology and an overview of environmental issues involving NO_x control.

The 4-day meeting was attended by persons from 14 nations. Forty-nine papers were presented by EPRI and EPA staff members, utility company representatives, boiler and related equipment manufacturers, research and development groups, and university representatives.

Symposium cochairpersons were David Eskinazi, Project Manager in the Air Quality Control Program of EPRI's Coal Combustion Systems Division; and James D. Kilgroe, Mechanical Engineer in the Combustion Research Branch of the EPA's Air and Energy Engineering Research Laboratory. Each of the cochairpersons made brief introductory remarks. Congressman Billy Tauzin of Louisiana delivered the keynote address. Written manuscripts were not prepared for the introductory remarks or keynote address; therefore, they are not published herein.

The Proceedings of the 1987 Joint Symposium have been compiled in two volumes. Volume 1 contains papers from the following sessions:

- Session I: Background and Environmental Issues
- Session II: Low-NO_x Combustion Development
- Session III: Manufacturers' Update of Commercially Available Technology
- Session IV: Coal-Fired Boiler Applications

Papers from the following sessions are contained in Volume 2:

- Session Va: Flue Gas Treatment
- Session Vb: Fundamental Combustion Studies
- Session VI: Cyclone-Fired Boilers
- Session VIIa: Oil- and Gas-Fired Boilers
- Session VIIb: Industrial and Commercial Applications

Also included in both volumes is an Appendix listing the Symposium attendees.

The assistance of Holly Rossi, Radian Corporation, in compiling these Proceedings is gratefully acknowledged.

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CURRENT STATUS OF SCR IN JAPAN

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ABSTRACT

Selective Catalytic Reduction of NO_x is widely applied to utility and industrial boilers in Japan. Among utility boilers, 99 units of them (approx. 110 million Nm³/h) have been equipped with SCR including 22 units of coal firing boilers (approx. 20 million Nm³/h). Among industrial boilers, 31 units of them (approx. 3.3 million Nm³/h) have also been applied with SCR (as of April 1986).

SCR installation started in 1977 for oil and gas and in 1979 for coal firing boilers. These operating experience suggested us that the cost and performance of SCR should be discussed again, because the catalyst itself (life, volume requirement, etc.) had been improved remarkably.

This paper will try to describe those facts from the utility standpoint.

1. Introduction

The selective catalytic reduction (SCR) method is one of the methods for NO_x reduction. The method is rather new and expensive, and most American utilities have shown a hesitation to the employment of the method.

The method, however, has many merits that the equipment is simple, no byproduct is produced and it is a dry process causing low temperature loss, and there has been a strong desire for clarifying some of its characteristics represented by the catalyst life, reduction of equipment cost and solutions to secondary troubles.

SCRs were installed early in Japan. As of April 1986, the experience in SCR operation is 6.5 years for coal firing boilers, 8.5 years for oil firing boilers and 8 years for LNG firing boilers.

At EPDC, SCR's have been used for A and B trains of Takehara No. 1 unit (250 MW) and for Takehara No. 3 unit (700 MW) among EPDC's 11 coal fired thermal power units, and they are operating since June 1981 and March 1983, respectively (that is, they are operating for the last 5 years and 3 years, respectively).

What we found about the catalyst from these experiences are described below.

<Catalyst life>

The definition of catalyst life is rather difficult. We therefore studied the period during which the SCR is operated without any additions or replacements to the initially loaded catalyst. Although there are some exceptions, it can be said that SCRs have been operated for more than 3 years for coal firing boilers, more than 4 to 7 years for oil firing boilers and more than 6 years for LNG firing boilers without any additions or replacements. These values are much larger than the value of 1 to 2 years which has conventionally been thought to be life of catalyst. In addition, these values are different from the so-called mean life of catalyst either, and the mean life would be much longer.

According to the experience at EPDC, it is known for the train A of Takehara No. 1 unit that the mean life of its catalyst (coal firing low dust system) is at least more than 4 years.

<Catalyst cost>

The method of cost calculation employed in Japan is different from that used in the U. S., the method of EPRI (CS-3603 Project 1256-7 Final Report October 1984 "SCR for coal fired power plants: feasibility and economics"*1) is used as the base.

For the case of 80% denitrification on inlet NO_x of 500 ppm, the EPRI calculation results in 11.7 mills/kWh for low sulfur coal and 8.8 mills/kWh for high sulfur coal. the EPDC calculation, on the other hand, results in 5.9 mills/kWh for low sulfur coal and 4.9 mills/kWh for high sulfur coal, which are about one-half of those of EPRI.

This is a result of simple calculation where EPDC used the catalyst life of 4 years while EPRI used the catalyst life of 1 year.

<Catalyst performance>

According to the development in the method of catalyst production, the pitch of honeycomb catalyst reduced from 10 mm to about 6 mm, and the effective catalytic area per unit volume (AP value) is much greater now. Therefore, the apparent catalyst requirement in volume has been reduced to about two-thirds.

The cost has also become lower correspondingly, and it is 5.2 mills/kWh for low sulfur coal.

In addition, we used to have problems of A/H troubles which came from ammonium bisulfate caused by slip NH₃ and SO₃, but such troubles as A/H clogging are fewer now due to the recent progress in the development of low SO₂ oxidation rate catalysts.

2. SCR Applications

2.1 Application to Utilities

All SCRs used at utilities in Japan are listed in Table 1. As of April 1986, 22 SCRs for coal firing boilers, 55 SCRs for oil firing boilers and 13 SCRs for LNG firing boilers are operating. It is considered that the reliability of SCR is demonstrated by the use of so many SCRs at Japanese utilities.

2.2 Japanese SCR Manufacturers

Mitsubishi Heavy Industries (MHI), Hitachi, Ltd. (HTC) (representing Babcock Hitachi (BHK)), Ishikawajima Harima Heavy Industries (IHI), Kawasaki Heavy Industries (KHI) and Hitachi Zosen (HZE) are the five Japanese manufacturers of SCRs for utilities.

Among other manufacturers, KHI may be known in the U. S. as it supplied SCRs to the Arapahoe Test Site of EPRI, Southern California Edison and City of San Diego in addition to contributing information to previous EPRI report "SCR for coal fired power plants: feasibility and economics."^{*1}

Table 2 shows the supply of SCRs to Japanese utilities, and Figure 1 shows the shares for coal firing boilers and those for all types of utility boilers.

However, these shares do not represent the quality of the SCR because it is common that the boiler manufacturer receives an order of SCR since it is considered as a part of the boiler.

3. Catalyst Life

3.1 First Replacement or Addition

It is very difficult to define the life of catalyst. If more catalyst than needed is charged initially, no replacement will be needed for a very long time. We should therefore look at the trend of deterioration in catalyst activity instead of the concept of life. This point will further be discussed later.

A rough measure we applied to consider the life of catalyst is to look at the period between the initial charge of catalyst and the subsequent catalyst replacement or addition.

Figures 2 to 4 show the starting time of operation and time of catalyst replacement or addition for all SCRs operating in Japan as relations between time on the abscissa and individual units on the ordinate. For each unit, the X-mark at the left end of the horizontal solid line corresponds to the starting time of SCR operation, and the length of the solid line corresponds to the period during which the SCR was operated without catalyst replacement or addition.

The right X-mark on the solid line indicates the time of catalyst replacement or addition and a dotted line follows the solid line after the X-mark.

X-marks on dotted line indicate that the catalyst was replaced or added at such points.

Solid lines up to April 1986 indicate that no catalyst replacement or addition took place for the unit.

It can roughly be said from these figures that SCRs for coal firing boilers are operated for 2 to 3 years, those for oil-firing boilers are operated for 4 to 7 years, and those for LNG firing boilers are operated for more than 6 years without catalyst replacement or addition although there are some exceptions.

The catalyst life is more than expected considering the manufacturers' guarantee period of 1 year at that time.

In Japan, it is an obligation to carry out a periodic inspection almost every year, and catalyst replacement or addition is carried out also during such

inspection if necessary. If there were no such restriction, the catalyst could be used much longer.

For the cases of coal firing boilers, the catalyst of first full capacity high dust SCR unit was replaced after about 2.5 years, but the high dust catalyst had been improved since then for longer life. In addition, the first full capacity low dust SCR units are the two units for the A and B trains of Takehara No. 1 unit. The catalyst of these units have been replaced or added for various test purposes, and it may be appropriate not to include these units in the statistics.

When these cases are excluded, SCRs for coal firing boilers are operated with the first catalyst for more than 3 years.

3.2 Concept of Mean Catalyst Life

In considering the concept of mean catalyst life, it is necessary to understand the catalyst activity, overall activity of multi-layer catalyst, actual trend of activity deterioration and the method of catalyst replacement.

<Catalyst activity>

As shown in Figure 5, the denitrification efficiency is expressed by the following formula, when the NH_3/NO_x molar ratio is 1 and the reaction is a linear reaction of NO_x concentration:

$$\eta = 1 - e^{-kt} \quad \text{-----} \quad (1)$$

where,

η : denitrification efficiency
 k : catalyst activity
 t : reaction time

<Overall activity of multi-layer catalyst>

As shown in Figure 6, the overall activity of multi-layer catalyst is equivalent to the sum of catalyst activities of component layers, and expressed by the following formula:

$$K = k_1 + k_2 + \dots + k_n \quad \text{-----} \quad (2)$$

where,

K : overall activity of n-layer catalyst
 $k_1, k_2, \dots, k_n$: catalyst activity of individual layers

When the catalyst consists of some catalyst layers of low activity and new catalyst layers, the overall denitrification efficiency can exceed a target value so far as the overall catalyst activity is greater than the design value.

<Actual trend of activity deterioration>

Figure 7 shows the trend of activity deterioration observed at Takehara No. 1A and 3. We could not obtain data on other power plants, but the trend can be similar.

<Method of catalyst replacement and addition>

To maintain an overall performance of catalyst layers is to maintain the overall activity above a certain level. With notion in mind, a variety of methods

for catalyst replacement and addition are considerable. For the purpose of discussion here, we consider two cases shown in Figure 8.

It is assumed that the amount of catalyst of which overall activity would drop to a target value in one year is charged in four layers. Case 1 is a method where all catalyst is replaced every year, and Case 2 is a method where another layer is added after one year. Figure 8 indicates that the annual catalyst consumption is $4 \times V$ for Case 1, and $1 \times V$ for Case 2. From the concept of mean catalyst life, the life for Case 2 is four years if the life for Case 1 is one year.

The catalyst activity has been measured up to only five years. The life at sixth and subsequent years is therefore an estimation, but the mean life can be extended much longer by employing a more intricate replacement method.

In addition, the mean life can be made longer by reducing the amount of annual replacement by increasing the number of catalyst layers.

<Mean catalyst life>

The concept of mean catalyst life becomes extremely difficult to grasp for multi-layer catalyst. It may be better therefore to consider the catalyst as a simple reagent, and think about its mean annual consumption in a certain period.

For this purpose, however, it is necessary to acquire data on the trend in activity deterioration for a much longer term. We do not have such data at present, and the mean life of four years obtained for Case 2 is used for calculation of economy in this paper.

4. Economy of SCR

4.1 Economy of SCR in the U. S.

As discussed in Section 1 Introduction, the levelized cost for 30 years reduces to about one half based on the EPRI report^{*1} when the mean life is change from one year to four years.

According to the report, the SCR cost as of December 1982 is as shown in Figure 9.

Among these, the case of inlet NO_x of 500 ppm (3% O₂ dry) and denitrification efficiency of 80% is also shown in Figure 9 for the case where the catalyst cost was reduced to one quarter.

For consideration of economy, other factors such as reduction of catalyst volume due to greater AP value (see <Catalyst performance> in Section 1 Introduction) and re-examination of the contingency factor due to increase of commercial applications, but it is found that the economy of SCR have greatly improved even when these factors are ignored.

5. Catalyst Performance

5.1 Performance Improvement by Change in Shape

The standard external dimensions of honeycomb type catalyst is 150W x 150L x 500H or x 1000H. The number of cells has increased along with the improvement in the manufacturing method. The cell configuration was 13 x 13 cells at first, but it has been improving to 15x15, 17x17, 20x20 and 21x21 cells. It is said that some manufacturers are developing a cell configuration of 35 x 35 cells.

It can be thought that the denitrification reaction is proportional to the area to which the flue gas makes contact with the catalyst in the direction of flow, and the area divided by the apparent volume becomes an important factor.

This value is called the AP value. In Figure 10, AP is expressed as follows:

$$AP = \frac{4 \times P \times n^2 \times H}{2 \times 2 \times H} \quad \text{-----} \quad (1)$$

$$\begin{aligned} 2 &= np + (n+1)t \\ &\approx n(p+t) \end{aligned} \quad \text{-----} \quad (2)$$

Thus,

$$AP \approx \frac{4P}{(p+t)^2} \quad \text{-----} \quad (3)$$

The AP value of each catalyst is shown in Table 3. If the performance of catalyst itself remains unchanged, the (apparent) required volume of catalyst changes when the number of cells is increased as also shown in Table 3.

That is, the required volume of 21x21-cell catalyst can only be 62% of that of 13x13-cell catalyst.

This fact not only allows to reduce the cost of catalyst itself but also those for reactors and other related devices.

Catalyst of finer cells may be more vulnerable to such problems as clogging and pressure loss, but EPDC replaced all pipe-type catalyst of Takehara No. 1B in November 1985 with 21x21-cell honeycomb catalyst and the SCR unit is operating in good condition since then.

5.2 Problem of A/H Clogging

The slip NH_3 is limited to 5 ppm or below at almost all plants for the purpose of avoiding the increase of differential pressure in A/H by acid ammonium sulfate.

At the same time, improvement of catalyst material is also going on to reduce the oxidation rate of SO_2 .

Figure 11 shows the correlation between the slip NH_3 and frequency of A/H washing observed at the latest low dust coal fired thermal power SCR (Takehara No. 3: 700 MW). The fuel coal mainly used at the power plant is low sulfur imported coal with a sulfur content of 0.6 to 0.8%. (SO_3 is 2 to 5 ppm.)

The abscissa represents the A/H washing interval (in months) and the ordinate represents the value of slip NH_3 .

It is clear that the A/H washing interval gets longer when slip NH_3 is lower.

6. Conclusions

As discussed above, the results of long-term SCR operation indicate unexpectedly long life, low cost and high performance.

EPDC intends to continue every effort for reduction of NO_x .

**Figure .1 Share of SCR manufactures for utility
coal firing boilers**



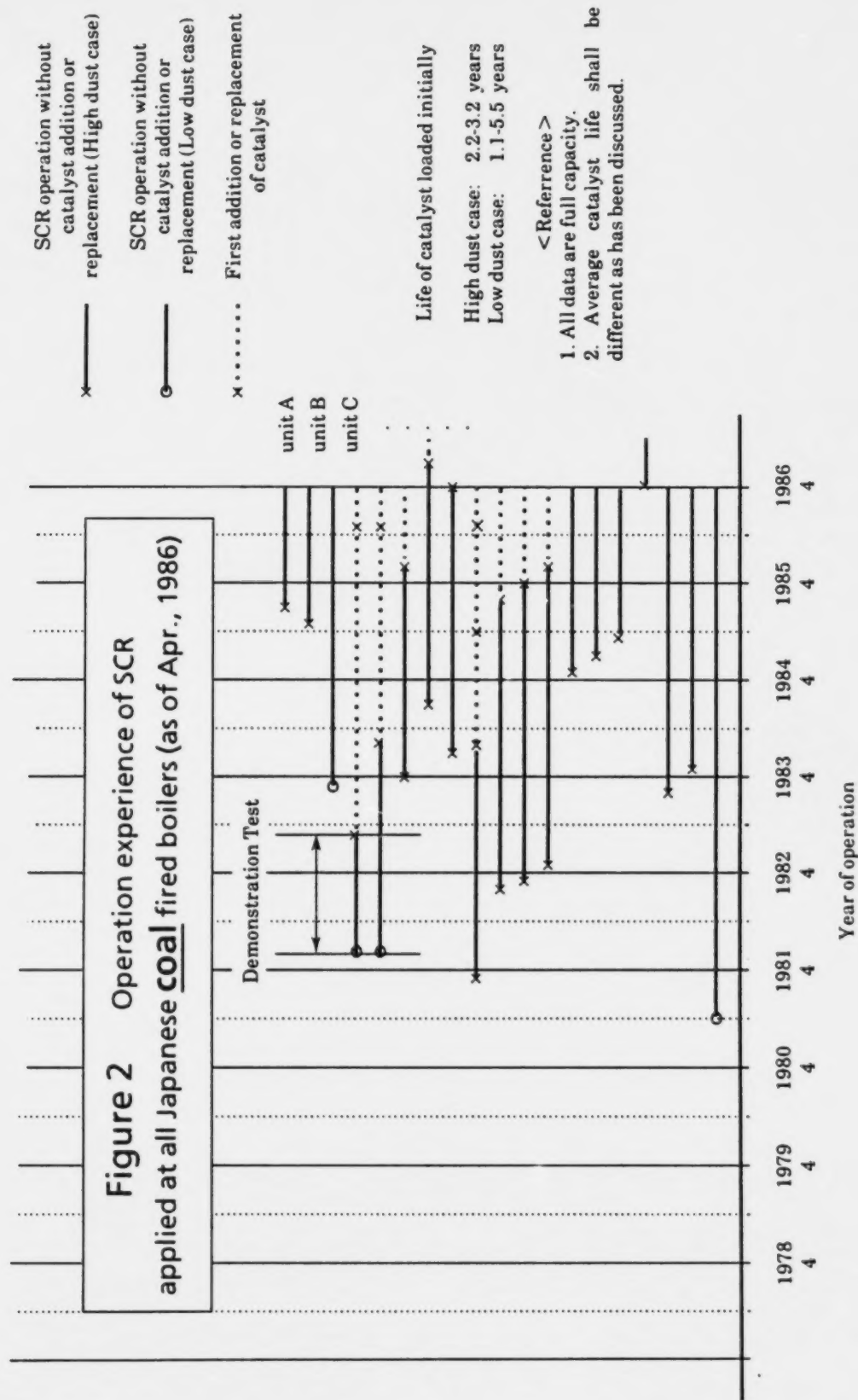
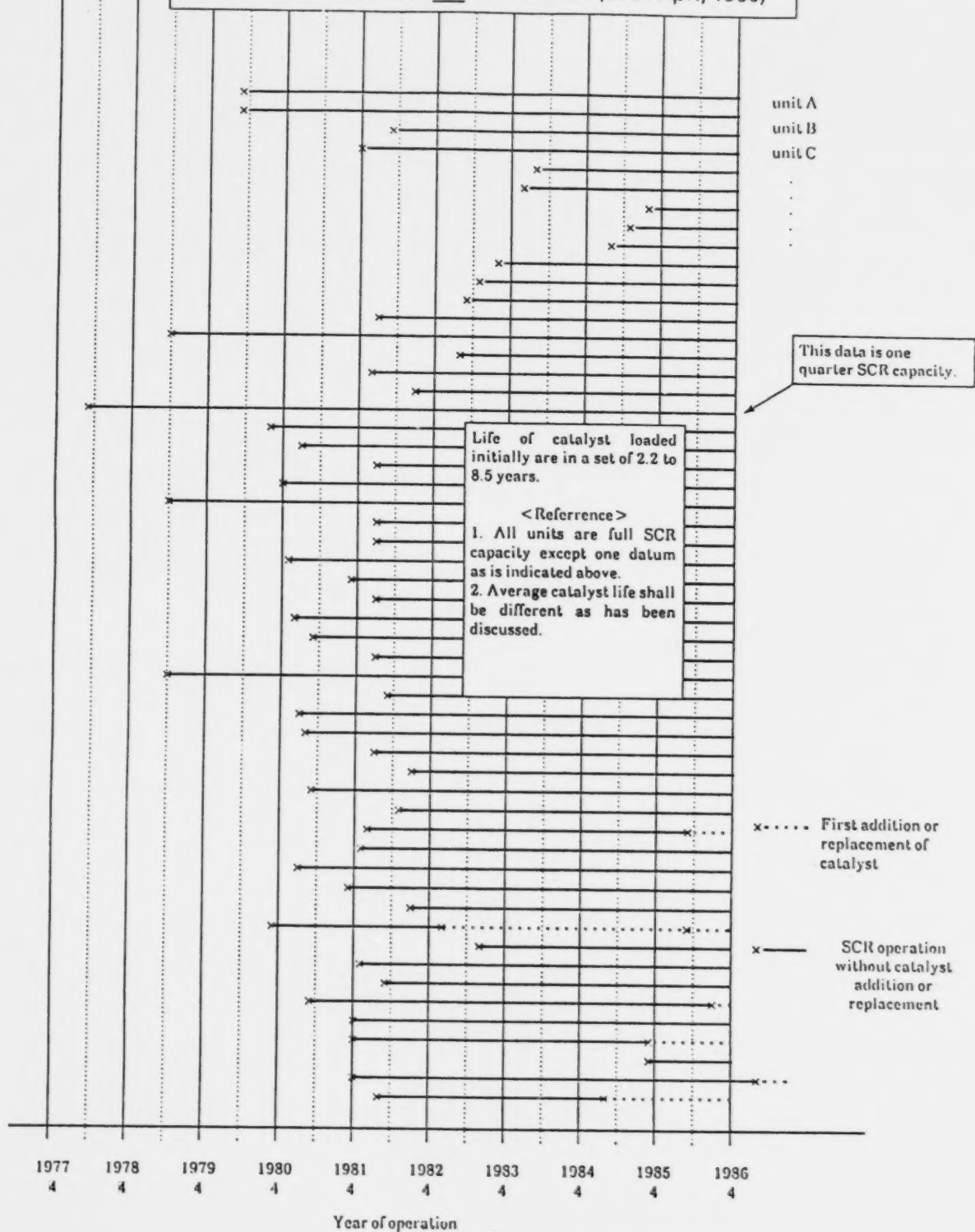


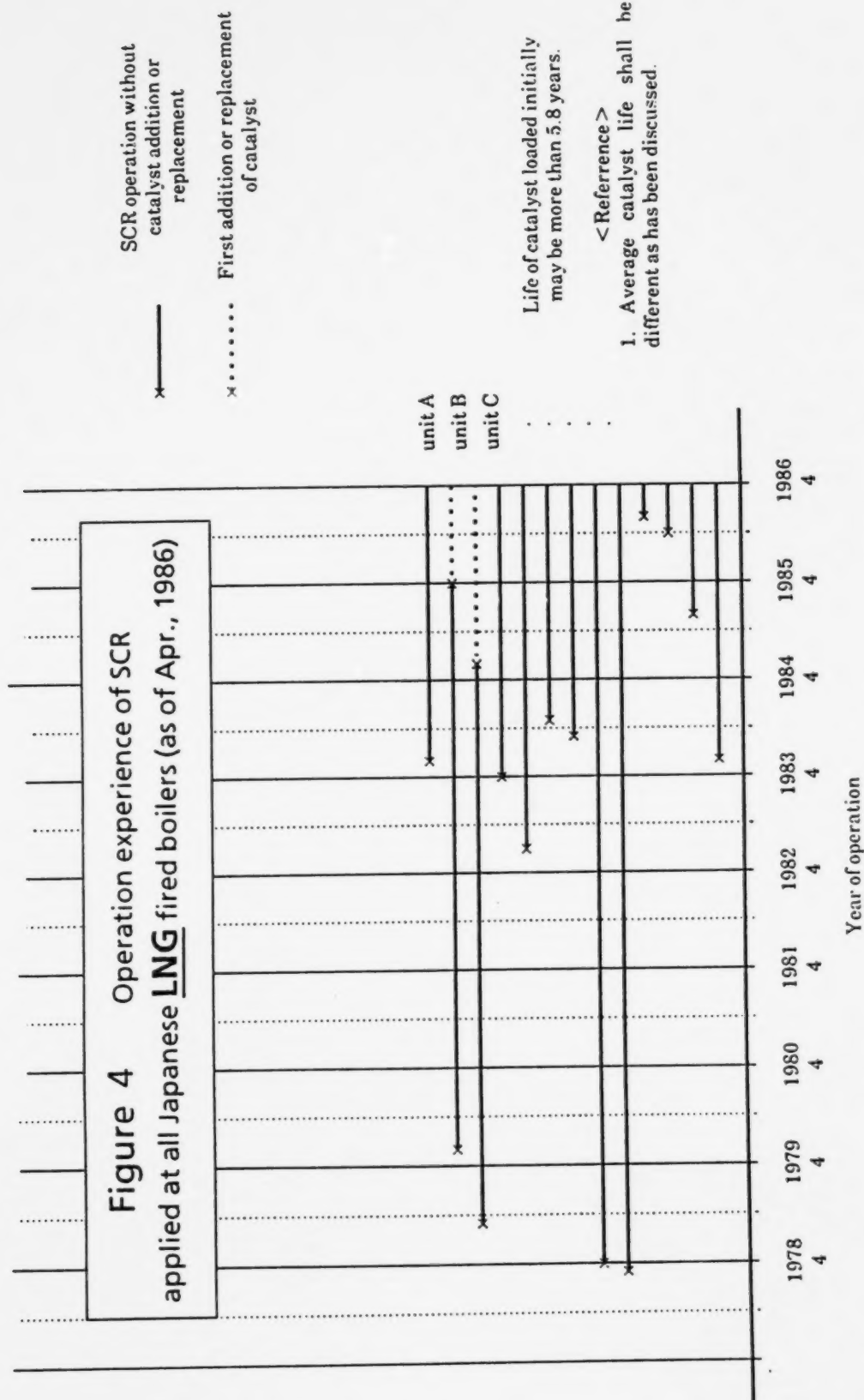
Figure 3 Operation experience of SCR applied at all Japanese oil fired boilers (as of Apr., 1986)



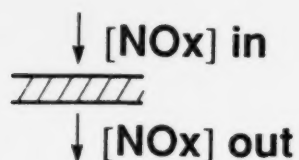
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Figure 4 Operation experience of SCR
applied at all Japanese LNG fired boilers (as of Apr., 1986)



* About $\eta = 1 - e^{-kt}$



When the NH_3/NOx molar ratio is 1, the reaction is a linear reaction of concentration:

$$\frac{d[\text{NOx}]}{dt} = -k [\text{NOx}]$$

where,

[NOx] : NOx concentration
k : catalyst activity
t : reaction time

Integrating the equation:

$$[\text{NOx}] = Ae^{-kt}$$

$$\eta = \frac{[\text{NOx}]_{\text{in}} - [\text{NOx}]_{\text{out}}}{[\text{NOx}]_{\text{in}}} = \frac{A - Ae^{-kt}}{A} = 1 - e^{-kt}$$

Thus,

$$\boxed{\eta = 1 - e^{-kt}}$$

Figure 5. Catalyst activity and DeNOx efficiency

	Vol.	Reaction Time	Catalyst Activity	DeNOx efficiency
Catalyst Layer 1	V	t	k_1	η_1
Catalyst Layer 2	V	t	k_2	η_2
...	...	...	...	...
Catalyst Layer n	V	t	k_n	η_n
Overall	V	t	K	η

N_i : NOx concentration

<Overall Activity>

$$\begin{aligned}
 1 - \eta &= \frac{N_n}{N_0} \\
 &= \frac{N_1}{N_0} \times \frac{N_2}{N_1} \times \dots \times \frac{N_n}{N_{n-1}} \\
 &= (1 - \eta_1) \times (1 - \eta_2) \times \dots \times (1 - \eta_n) \\
 &= e^{-(k_1 + k_2 + \dots + k_n)t} \\
 &= e^{-Kt}
 \end{aligned}$$

<Each Activity>

$$\begin{aligned}
 1 - \eta_1 &= \frac{N_1}{N_0} = e^{-k_1 t} \\
 1 - \eta_2 &= \frac{N_2}{N_1} = e^{-k_2 t} \\
 &\vdots \\
 1 - \eta_n &= \frac{N_n}{N_{n-1}} = e^{-k_n t}
 \end{aligned}$$

Then

$$K = k_1 + k_2 + \dots + k_n$$

Figure 6. Overall activity in case of multiple layer

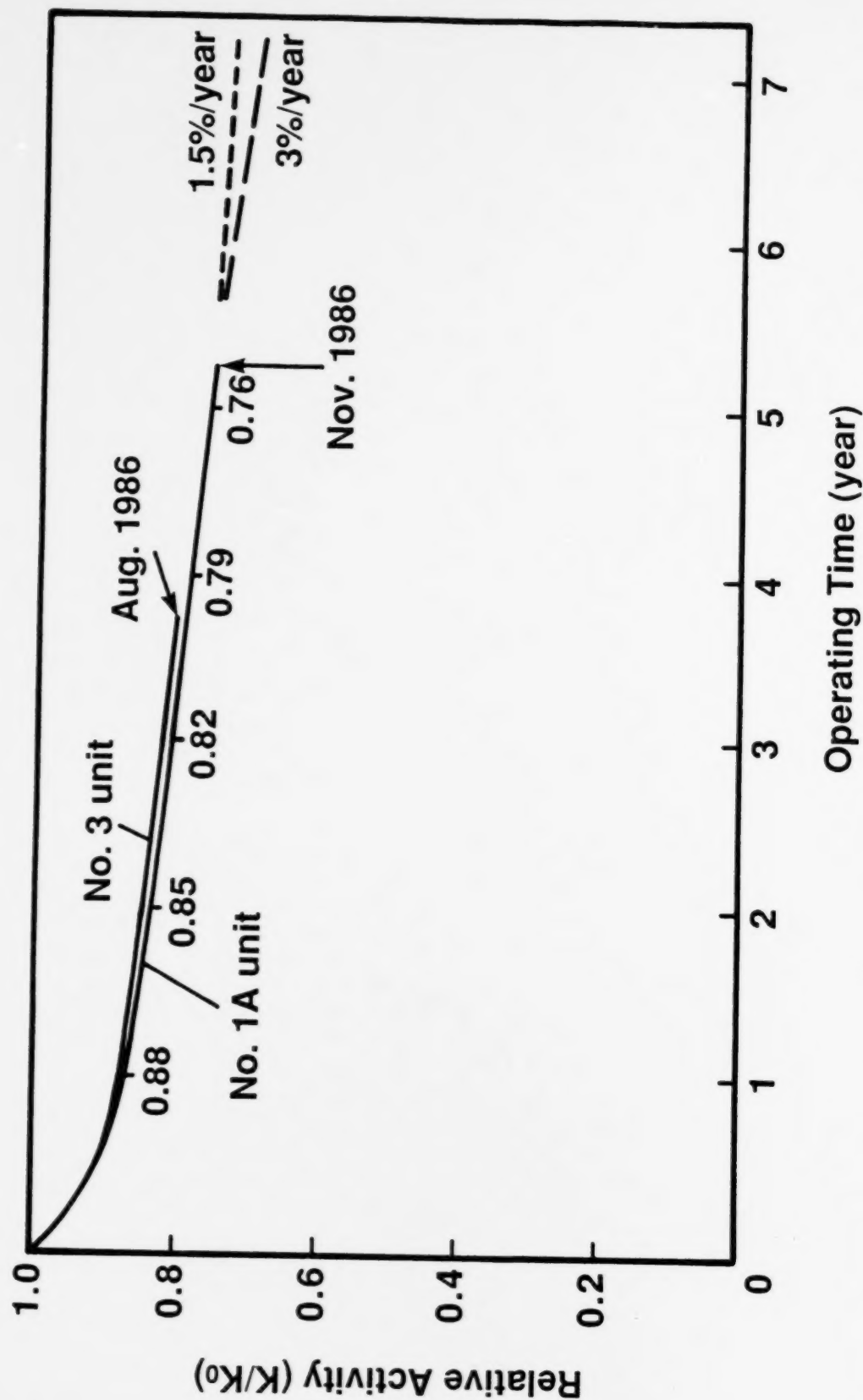
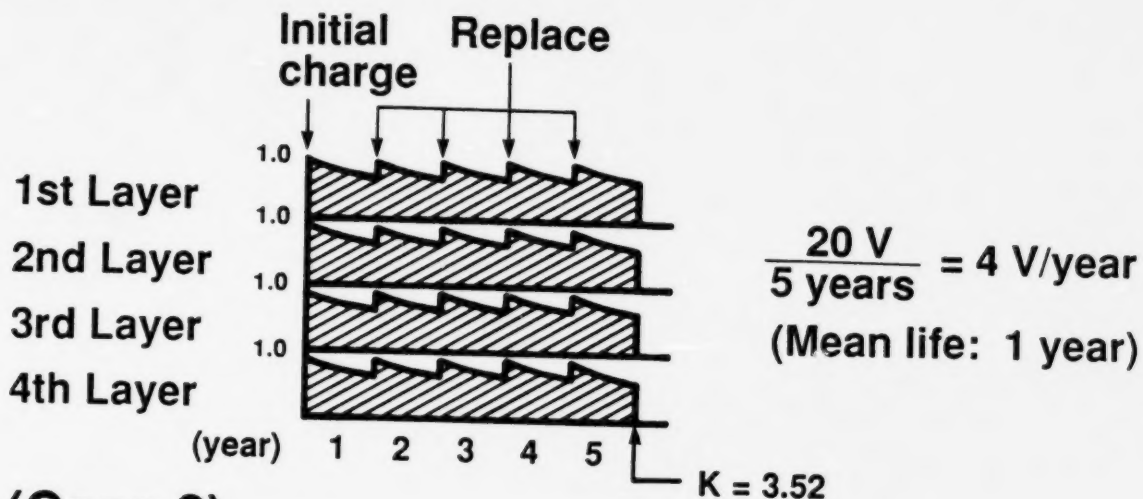


Figure 7. Deterioration of relative activity of catalyst (Takehara No. 1A and 3)

<Replacing Method>

Initial charge of catalyst : 1-year requirement
 Number of layers : 4 or 5

(Case 1)



(Case 2)

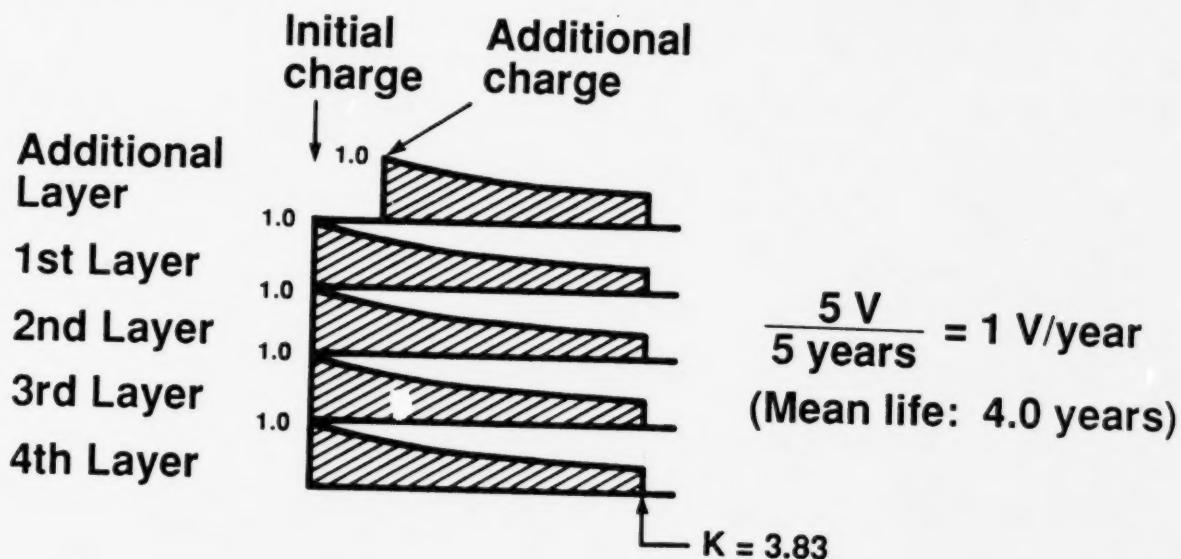
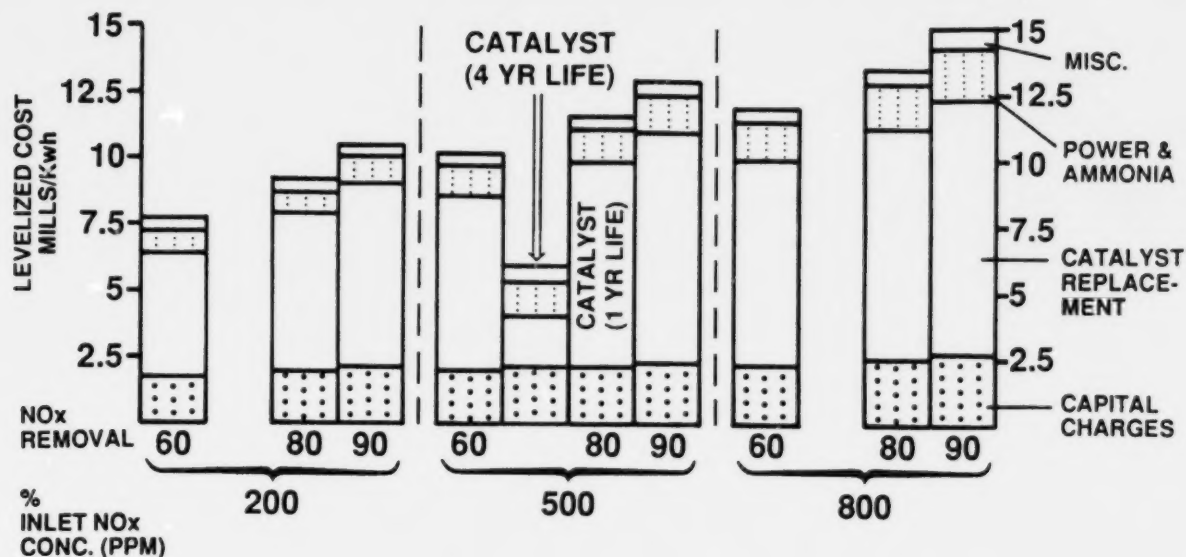
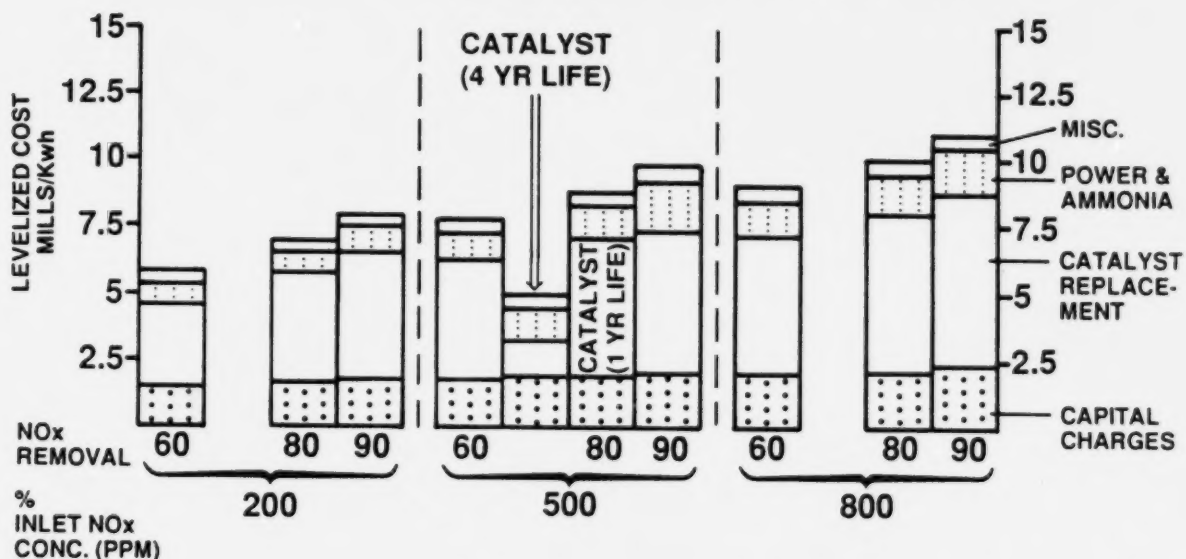


Figure 8. Catalyst life v.s. replacing method



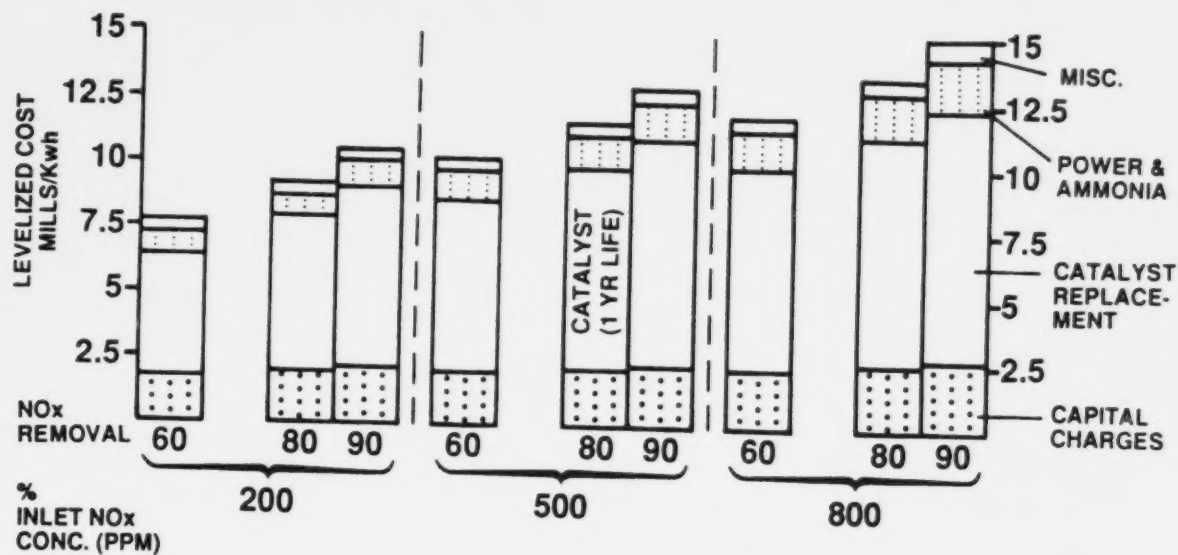
A. Low Sulfur Coal Application Total Levelized Cost Components



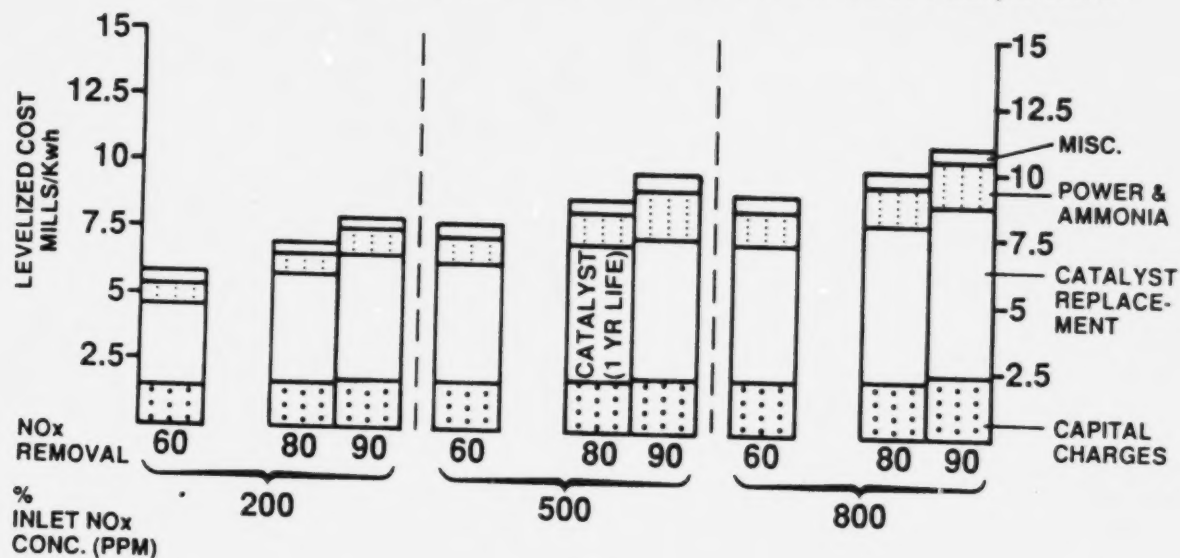
B. High Sulfur Coal Application Total Levelized Cost Components

(EPRI CS-3603 Project 1256-7 Final Report October 1984
 "Selective Catalytic Reduction for Coal-fired Power Plant:
 Feasibility and Economics")

Figure 9. SCR economics based on 4 year's life of catalyst



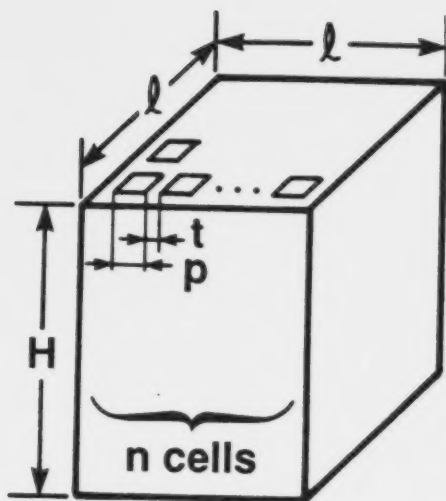
A. Low Sulfur Coal Application Total Levelized Cost Components



B. High Sulfur Coal Application Total Levelized Cost Components

(EPRI CS-3603 Project 1256-7 Final Report October 1984
"Selective Catalytic Reduction for Coal-fired Power Plant:
Feasibility and Economics")

Figure 9. SCR economics based on 4 year's life of catalyst



p : pitch
t : wall thickness
n : number of cells

Left drawing shows
 $n \times n$ cells honeycomb
 type catalyst

Catalyst surface area : $4 \times p \times n^2 \times H \text{ (m}^2\text{)}$

Catalyst outward volume : $l \times l \times H \text{ (m}^3\text{)}$

$$AP = \frac{4 \times p \times n^2 \times H}{l \times l \times H}$$

Figure 10. AP value and catalyst configuration

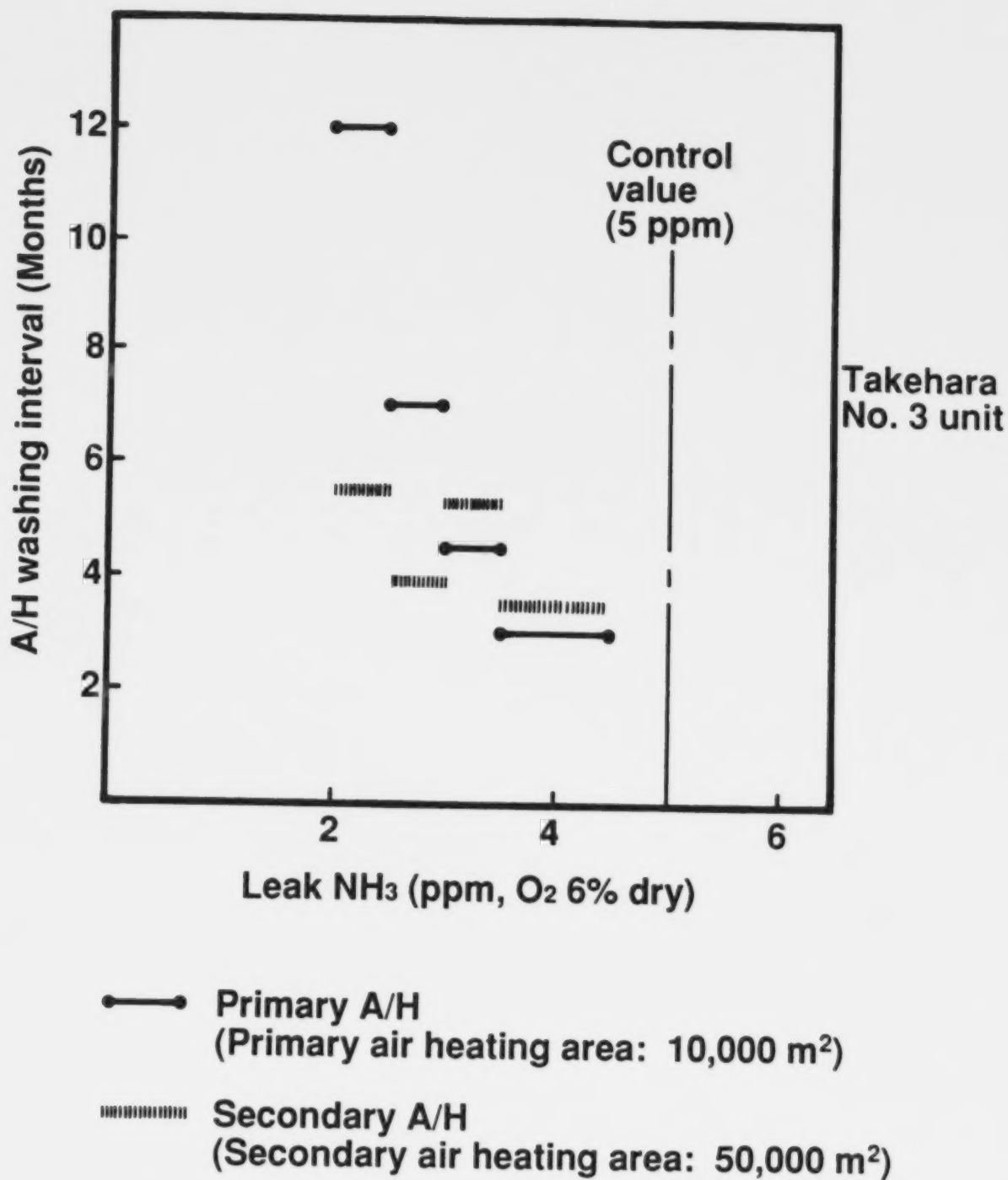


Figure 11. Interval of scheduled A/H water washing v.s. slip NH_3

Table 1-(1) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986,4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commi-ssioning Date (Plan-ning)	DeNOx Facility	Treated Gas Vol. (m ³ N/h)	Treated /Total Gas Ratio (%)	Manu-facturer	DeNOx Effi-ciency	Commiss-ioning Date of DeNOx Facility
1	Hokkaido	Tomatou-Atsuma	1	350	Coal	10/80	SCR (Plate)	280,000	25	HTC	80	10/80
2	Touhoku	Sendai	2	175	Coal	11/60	SCR (Plate)	549,000	100	HTC	60	5/83
3	Touhoku	Sendai	3	175	Coal	6/62	SCR (Plate)	549,000	100	HTC	60	2/83
4	Tohoku	Higashi-Niigata	2	600	LNG	6/83	SCR (Honeycomb)	1,700,000	100	IHI	62	6/83
5	Tohoku	Higashi-Niigata	3-1~3-3	1090/2	LNG Combined	10/85	SCR (Honeycomb)	7,700,000/2	100	MHI	80	12/84
6	Tohoku	Higashi-Niigata	3-4~3-6	1090/2	LNG Combined	10/85	SCR (Honeycomb)	7,700,000/2	100	MHI	80	10/85
7	Tokyo	Yokohama	1	175	Crude, Heavy Oil LNG	8/62	SCR (Plate)	531,000	100	HTC	≈ 30	4/81
8	Tokyo	Yokohama	3	175	Crude, Heavy Oil LNG	4/63	SCR (Plate)	531,000	100	HTC	≈ 30	3/85
9	Tokyo	Ohai	2	350	Oil	2/72	SCR (Honeycomb)	1,020,000	700	IHI	≈ 30	4/81
10	Tokyo	Yokosuka	1	265	COM Heavy Oil	10/60	SCR (Honeycomb)	875,000	100	MHI	70	2/85
11	Tokyo	Yokosuka	2	265	COM Heavy Oil	9/62	SCR (Honeycomb)	875,000	100	MHI	70	5/85
12	Tokyo	Yokosuka	4	350	Crude, Heavy Oil	7/64	SCR (Honeycomb)	1,076,000	100	MHI	≈ 10	8/81

Reference ; Facility of Thermal Power Plants in Japan- Engineering Dept, The Federation of Electric Power Companies

Table 1-(2) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986,4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commissioning Date (Planning)	DeNOx Facility	Treated Gas Vol. (m ³ /h)	Treated /Total Gas Ratio (%)	Manufacturer	DeNOx Efficiency	Commissioning Date of DeNOx Facility
13	Tokyo	Futtsu	1-1-1-7	1000	LNG	12/85~11/86	SCR (Honeycomb)	8,000,000	100	H2C	80	12/85~(11/86)
14	Tokyo	Futtsu	2-1-2-7	1000	LNG	(2/88)~(11/88)	SCR (Honeycomb)	8,000,000	100	H2C	80	(2/88)~(11/88)
15	Tokyo	Higashi-Ongishima	1	1000	LNG	(9/87)	SCR	2,770,000	100	HTC	80	(9/87)
16	Tokyo	Higashi-Ongishima	2	1000	LNG	(9/89)	SCR	2,770,000	100	-	80	(9/89)
17	Chubu	Shin-Nagoya	2	220	Heavy Oil	2/60	SCR (Honeycomb)	670,000	100	MHI	33	4/81
18	Chubu	Shin-Nagoya	3	220	Heavy Oil	3/61	SCR (Honeycomb)	650,000	100	MHI	33	9/80
19	Chubu	Shin-Nagoya	5	220	Heavy Oil	1/64	SCR (Honeycomb)	640,000	100	MHI	33	9/81
20	Chubu	Shin-Nagoya	6	220	Heavy Oil	7/64	SCR (Honeycomb)	640,000	100	MHI	29	5/81
21	Chubu	Chita	1	375	Crude, Heavy Oil LNG	2/66	SCR (Honeycomb)	1,100,000	100	MHI	48	12/82
22	Chubu	Chita	2	375	Crude, Heavy Oil LNG	1/67	NCR	1,036,000	100	MHI	40	1/77
23	Chubu	Chita	4	700	Crude, Heavy Oil LNG	3/74	SCR (Honeycomb)	1,960,000	100	MHI	80	3/80
24	Chubu	Chita	5	700	LNG	3/78	SCR (Pellet)	1,910,000	100	HTC	80	3/78
25	Chubu	Chita	6	700	LNG	4/78	SCR (Pellet)	1,910,000	100	HTC	80	4/78

Reference : Facility of Thermal Power Plants in Japan - Engineering Dept., The Federation of Electric Power Companies

Table 1-(3) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986,4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commissioning Date (Planning)	DeNOx Facility	Treated Gas Vol. (m ³ /h)	Treated /Total Gas Ratio (%)	Manufacturer	DeNOx Efficiency	Commissioning Date of DeNOx Facility
26	Chubu	Nishi-Nagoya	3	375	Crude, Heavy Oil	7/72	SCR (Plate)	1,000,000	100	HTC	80	12/81
27	Chubu	Nishi-Nagoya	4	375	Crude, Heavy Oil	9/72	SCR (Plate)	1,000,000	100	HTC	80	3/81
28	Chubu	Nishi-Nagoya	5	500	Crude, Heavy Oil	10/74	SCR (Honeycomb)	1,360,000	100	MHI	70	(10/86)
29	Chubu	Nishi-Nagoya	6	500	Crude, Heavy Oil	4/75	SCR (Honeycomb)	1,340,000	100	IHI	80	7/80
30	Chubu	Atsumi	3	700	Crude, Heavy Oil	5/81	SCR (Honeycomb)	1,900,000	100	MHI	80	5/81
31	Chubu	Atsumi	4	700	Crude, Heavy Oil	6/81	SCR (Honeycomb)	1,900,000	100	MHI	80	6/81
32	Chubu	Chita-Daini	1	700	LNG	9/83	SCR (Pellet)	1,910,000	100	HTC	80	9/83
33	Chubu	Chita-Daini	2	700	LNG	11/83	SCR (Pellet)	1,910,000	100	IHI	80	11/83
34	Chubu	Yokkaichi	4-1 ~ 4-5	560	LNG LPG	(7/88)	SCR (Honeycomb)	4,300,000	100	Toshiba	80	(7/88)
35	Chubu	Owase-Mita	3	500	Crude, Heavy Oil	(3/87)	SCR (Plate)	1,370,000	100	HTC	80	(3/87)
36	Hokuriku	Toyama-Shinkou	2	500	Crude, Heavy Oil	11/81	SCR (Honeycomb)	1,350,000	100	IHI	80	11/81
37	Kansai	Sakai-Kou	1	250	Crude, Heavy Oil LNG	12/64	SCR (Honeycomb)	800,000	100	MHI	75	9/80
38	Kansai	Sakai-Kou	2	250	Crude, Heavy Oil LNG	8/65	SCR (Honeycomb)	800,000	100	MHI	75	1/82

Reference ; Facility of Thermal Power Plants in Japan- Engineering Dept, The Federation of Electric Power Companies

Table 1-(3) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986,4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commi-ssioning Date (Plan-ning)	DeNOx Facility	Treated Gas Vol. (m ³ /h)	Treated /Total Gas Ratio (%)	Manu-facturer	DeNOx Effi-ciency	Commiss-ioning Date of DeNOx Facility
26	Chubu	Nishi-Nagoya	3	375	Crude, Heavy Oil	7/72	SCR (Plate)	1,000,000	100	HTC	80	12/81
27	Chubu	Nishi-Nagoya	4	375	Crude, Heavy Oil	9/72	SCR (Plate)	1,000,000	100	HTC	80	3/81
28	Chubu	Nishi-Nagoya	5	500	Crude, Heavy Oil	10/74	SCR (Honeycomb)	1,360,000	100	MHI	70	(10/86)
29	Chubu	Nishi-Nagoya	6	500	Crude, Heavy Oil	4/75	SCR (Honeycomb)	1,340,000	100	IHI	80	7/80
30	Chubu	Atsumi	3	700	Crude, Heavy Oil	5/81	SCR (Honeycomb)	1,900,000	100	MHI	80	5/81
31	Chubu	Atsumi	4	700	Crude, Heavy Oil	6/81	SCR (Honeycomb)	1,900,000	100	MHI	80	6/81
32	Chubu	Chita-Daini	1	700	LNG	9/83	SCR (Pellet)	1,910,000	100	HTC	80	9/83
33	Chubu	Chita-Daini	2	700	LNG	11/83	SCR (Pellet)	1,910,000	100	IHI	80	11/83
34	Chubu	Yokkaichi	4-1 ~ 4-5	560	LNG LPG	(7/88)	SCR (Honeycomb)	4,300,000	100	Toshiba	80	(7/88)
35	Chubu	Owase-Mita	3	500	Crude, Heavy Oil	(3/87)	SCR (Plate)	1,370,000	100	HTC	80	(3/87)
36	Hokuriku	Toyama-Shinkou	2	500	Crude, Heavy Oil	11/81	SCR (Honeycomb)	1,350,000	100	IHI	80	11/81
37	Kansai	Sakai-Kou	1	250	Crude, Heavy Oil LNG	12/64	SCR (Honeycomb)	800,000	100	MHI	75	9/80
38	Kansai	Sakai-Kou	2	250	Crude, Heavy Oil LNG	8/65	SCR (Honeycomb)	800,000	100	MHI	75	1/82

Reference; Facility of Thermal Power Plants in Japan-Engineering Dept, The Federation of Electric Power Companies

Table 1-(4) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986,4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commissioning Date (Planning)	DeNOx Facility	Treated Gas Vol. (m ³ /h)	Treated Gas Ratio (%)	Manufacturer	DeNOx Efficiency	Commissioning Date of DeNOx Facility
39	Kansai	Sakai-Kou	4	250	Crude, Heavy Oil LNG	3/67	SCR (Honeycomb)	800,000	100	MHI	75	7/81
40	Kansai	Sakai-Kou	5	250	Crude, Heavy Oil LNG	10/67	SCR (Plate)	800,000	100	HTC	75	8/80
41	Kansai	Sakai-Kou	6	250	Crude, Heavy Oil LNG	2/68	SCR (Honeycomb)	800,000	100	MHI	75	7/80
42	Kansai	Sakai-Kou	7	250	Crude, Heavy Oil LNG	10/70	SCR (Honeycomb)	800,000	100	MHI	75	9/81
43	Kansai	Osaka	1	156	Crude, Heavy Oil	4/59	SCR (Honeycomb)	530,000	100	MHI	30	10/78
44	Kansai	Osaka	2	156	Crude, Heavy Oil	10/59	SCR (Honeycomb)	530,000	100	MHI	75	8/81
45	Kansai	Osaka	3	156	Crude, Heavy Oil	2/60	SCR (Honeycomb)	530,000	100	MHI	75	9/80
46	Kansai	Osaka	4	156	Crude, Heavy Oil	3/60	SCR (Honeycomb)	530,000	100	MHI	75	6/80
47	Kansai	Tanagawa	3	156	Crude, Heavy Oil	4/63	SCR (Honeycomb)	520,000	100	MHI	75	8/81
48	Kansai	Tanagawa	4	156	Crude, Heavy Oil	10/63	SCR (Honeycomb)	520,000	100	MHI	75	3/81
49	Kansai	Kasugade	1	156	Crude, Heavy Oil	10/63	SCR (Honeycomb)	470,000	100	IHI	30	5/80
50	Kansai	Kasugade	2	156	Crude, Heavy Oil	1/64	SCR (Honeycomb)	470,000	100	IHI	30	8/81
51	Kansai	Tanagawa-Daini	2	600	Crude, Heavy Oil	8/77	SCR (Plate)	1,520,000	100	HTC	75	8/81

Reference ; Facility of Thermal Power Plants in Japan-Engineering Dept., The Federation of Electric Power Companies

Table 1-(5) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986.4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commi-ssioning Date (Plan-ning)	DeNOx Facility	Treated Gas Vol. (m ³ N/h)	Treated /Total Gas Ratio (%)	Manu-facturer	DeNOx Effi-ciency	Commiss-ioning Date of DeNOx Facility
52	Kansai	Amazaki-Higashi	1	156	Heavy Oil	9/65	SCR(Plate)	470,000	100	HTC	30	10/78
53	Kansai	Amazaki-Higashi	2	156	Heavy Oil	10/66	SCR (Plate)	470,000	100	HTC	30	4/80
54	Kansai	Amazaki-Daisan	1	156	Crude, Heavy Oil	1/63	SCR (Plate)	470,000	100	HTC	30	8/81
55	Kansai	Amazaki-Daisan	2	156	Crude, Heavy Oil	5/63	SCR (Plate)	470,000	100	HTC	30	7/80
56	Kansai	Amazaki-Daisan	3	156	Crude, Heavy Oil	9/69	SCR (Plate)	450,000	100	HTC	30	2/80
57	Kansai	Kainan	1	450	Crude, Heavy Oil	5/70	SCR (Plate)	300,000	25	HTC	75	9/77
58	Kansai	Kainan	3	600	Crude, Heavy Oil	4/74	SCR (Honeycomb)	1,640,000	100	MHI	75	1/82
59	Kansai	Kainan	4	600	Crude, Heavy Oil	6/73	SCR (Plate)	1,645,000	100	HTC	75	6/81
60	Kansai	Himeji-Daiichi	1	33	Heavy Oil	9/55	SCR (Honeycomb)	160,000	100	IHI	Heavy Oil 75 Coal 80	9/82
61	Kansai	Himeji-Daiichi	5	156	Heavy Oil	7/62	SCR (Honeycomb)	490,000	100	IHI	30	10/78
62	Kansai	Himeji-Daini	6	600	Crude, Heavy Oil LPG	11/73	SCR (Honeycomb)	1,620,000	100	IHI	Crude, Heavy Oil 75 LNG 80	8/81
63	Kansai	Aioi	1	375	Crude, Heavy Oil	9/82	SCR (Honeycomb)	1,060,000	100	IHI	75	9/82
64	Kansai	Aioi	2	375	Crude, Heavy Oil	11/82	SCR (Honeycomb)	1,060,000	100	IHI	75	11/82

Reference ; Facility of Thermal Power Plants in Japan- Engineering Dept, The Federation of Electric Power Companies

Table 1-(6) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986,4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commissioning Date (Planning)	DeNOx Facility	Treated Gas Vol. (m ³ /h)	Treated Gas Ratio (%)	Manufacturer	DeNOx Efficiency	Commissioning Date of DeNOx Facility
65	Kansai	Aioi	3	375	Crude, Heavy Oil	1/83	SCR (Honeycomb)	1,060,000	100	IHI	75	1/83
66	Kansai	Nan-Kou	1	600	LNG	(11/89)	SCR (Honeycomb)	1,759,000	100	-	80	(11/89)
67	Kansai	Nan-Kou	2	600	LNG	(5/90)	SCR (Honeycomb)	1,759,000	100	-	80	(5/90)
68	Kansai	Nan-Kou	3	600	LNG	(11/90)	SCR (Honeycomb)	1,759,000	100	-	80	(11/90)
69	Kansai	Gobou	1	600	Crude, Heavy Oil	9/84	SCR (Honeycomb)	1,600,000	100	MHI	75	9/84
70	Kansai	Gobou	2	600	Crude, Heavy Oil	11/84	SCR (Plate)	1,600,000	100	HTC	75	11/84
71	Kansai	Gobou	3	600	Crude, Heavy Oil	3/85	SCR (Honeycomb)	1,600,000	100	MHI	75	3/85
72	Kansai	Akou	1	600	Crude, Heavy Oil	(8/87)	SCR (Honeycomb)	1,600,000	100	MHI	80	(8/87)
73	Kansai	Akou	2	600	Crude, Heavy Oil	(12/87)	SCR (Honeycomb)	1,600,000	100	IHI	80	(12/87)
74	Kansai	Miyazu Energy Laboratory	1	375	Crude, Heavy Oil	(8/89)	SCR (Honeycomb)	977,400	100	MHI	80	(8/89)
75	Kansai	Miyazu Energy Laboratory	2	375	Crude, Heavy Oil	(12/89)	SCR (Honeycomb)	986,100	100	KHI	80	(12/89)
76	Cyugoku	Mizushima	1	125	Coal	11/61	SCR (Plate)	450,000	100	HTC	65	7/84
77	Cyugoku	Mizushima	2	156	Coal	8/63	SCR (Plate)	540,000	100	HTC	65	5/84

Reference : Facility of Thermal Power Plants in Japan - Engineering Dept., The Federation of Electric Power Companies

Table 1-(7) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986,4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commissioning Date (Planning)	DeNOx Facility	Treated Gas Vol. (m ³ /h)	Treated Gas /Total Gas Ratio (%)	Manufacturer	DeNOx Efficiency	Commissioning Date of DeNOx Facility
78	Cyugoku	Mizushima	3	350	Crude, Heavy Oil	2/73	SCR(Plate)	950,000	100	HTC	80	6/83
79	Cyugoku	Tamashima	1	350	Crude, Heavy Oil	3/71	SCR (Plate)	950,000	100	HTC	80	8/83
80	Cyugoku	Iwakuni	2	350	Crude, Heavy Oil	4/72	SCR (Honeycomb)	980,000	100	MHI	80	4/81
81	Cyugoku	Iwakuni	3	500	Crude, Heavy Oil LPG	9/81 3/82	SCR (Honeycomb)	1,400,000	100	MHI	80	9/81
82	Cyugoku	Kudamatsu	2	375	Crude, Heavy Oil	7/73	SCR (Honeycomb)	1,050,000	100	IHI	80	9/79
83	Cyugoku	Kudamatsu	3	700	Crude, Heavy Oil	9/79	SCR (Honeycomb)	1,900,000	100	IHI	80	9/79
84	Cyugoku	Shin-Ube	1	75	Coal	8/58	SCR (Honeycomb)	300,000	100	MHI	65	5/82
85	Cyugoku	Shin-Ube	2	75	Coal	5/59	SCR (Honeycomb)	300,000	100	MHI	65	3/82
86	Cyugoku	Shin-Ube	3	156	Coal	6/62	SCR (Honeycomb)	580,000	100	MHI	65	2/82
87	Cyugoku	Shin-Onoda	1	500	Coal	4/86	SCR (Honeycomb)	1,600,000	100	IHI	80	4/86
88	Cyugoku	Shin-Onoda	2	500	Coal	(2/87)	SCR (Honeycomb)	1,600,000	100	IHI	80	(2/87)
89	Cyugoku	Shimonoseki	1	175	Coal	3/67	SCR (Honeycomb)	550,000	100	MHI	50	3/81
90	Shikoku	Saijo	1	156	Coal	11/65	SCR (Honeycomb)	550,000	100	MHI	65	7/83

Reference ; Facility of Thermal Power Plants in Japan- Engineering Dept, The Federation of Electric Power Companies

Table 1-(8) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986,4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commissioning Date (Planning)	DeNOx Facility	Treated Gas Vol. (m ³ /h)	Treated /Total Gas Ratio (%)	Manufacturer	DeNOx Efficiency	Commissioning Date of DeNOx Facility
91	Shikoku	Saijo	2	250	Coal	1/84	SCR (Honeycomb)	800,000	100	IHI	65	1/84
92	Kyushu	Shin-Kokura	1	156	LNG	10/61	SCR (Honeycomb)	442,000	100	MHI	80	7/82
93	Kyushu	Shin-Kokura	2	156	LNG	11/62	SCR (Honeycomb)	484,000	100	KHI	80	4/83
94	Kyushu	Shin-Kokura	3	600	LNG	9/78	SCR (Pellet)	1,690,000	100	MHI	80	9/78
95	Kyushu	Shin-Kokura	4	600	LNG	6/79	SCR (Pellet)	1,690,000	100	MHI	80	6/79
96	Kyushu	Shin-Kokura	5	600	LNG	7/83	SCR	1,620,000	100	MHI	80	7/83
97	Kyushu	Minato	1	156	Coal	9/60	SCR (Honeycomb)	516,000	100	MHI	50	4/83
98	Kyushu	Matsuura	1	700	Coal	(7/89)	SCR (Honeycomb)	2,207,000	100	-	80	(7/89)
99	Kyushu	Shin-Ohita	1.1~1.6	690	LNG	(7/91)	SCR (Plate)	5,400,000	100	-	80	(7/91)
100	EPDC	Takehara	1	250	Coal	7/67	SCR (Plate,Pipe)	815,000	100	HTC KHI	80	10/82
101	EPDC	Takehara	3	700	Coal	3/83	SCR (Plate)	2,320,000	100	HTC	80	3/83
102	EPDC	Matsuura	1	1000	Coal	(7/90)	SCR	3,029,000	100	-	80	(7/90)
103	Sakata	Sakata	1	350	Coal	9/84	SCR (Honeycomb)	1,140,000	100	MHI	28	9/84

Reference ; Facility of Thermal Power Plants in Japan- Engineering Dept., The Federation of Electric Power Companies

Table 1-(9) List of DeNOx Facilities for Utility Boiler in Japan (As of 1986.4)

No.	Company	P/S	Unit No.	Output (MW)	Fuel	Commissioning Date (Planning)	DeNOx Facility	Treated Gas Vol. (m ³ N/h)	Treated /Total Gas Ratio (%)	Manufacturer	DeNOx Efficiency	Commissioning Date of DeNOx Facility
104	Sakata	Sakata	2	350	Heavy Oil	10/78	SCR (Honeycomb)	1,140,000	100	MHI	28	N/A
105	Joban	Nakoso	8	600	Coal Heavy Oil	9/83	SCR (Honeycomb)	1,800,000	100	MHI	60	9/83
106	Joban	Nakoso	9	600	Coal Heavy Oil	12/83	SCR (Honeycomb)	1,800,000	100	IHI	60	12/83
107	Toyama	Toyama Sinkou	1	250	Coal	9/71	SCR (Plate)	690,000	100	HTC	60	11/84
108	Toyama	Toyama Sinkou	2	250	Coal	6/72	SCR (Plate)	690,000	100	HTC	60	12/84
109	Tobata	Tobata	4	375	Natural Gas from Coke, Blast and Converting Furnace	3/78	SCR (Honeycomb)	1,563,800	-	MHI	60	6/81

Reference ; Facility of Thermal Power Plants in Japan - Engineering Dept, The Federation of Electric Power Companies

Table 2 SCR manufacturers for utility boilers in Japan
(units: as of April 1986)

	MHI	HTC	IHI	KHI	HZC	Total
coal	9	9.5	3	0.5	0	22
oil	26	16	13	0	0	55
LNG	6	3	2	1	1	13
Total	41	28.5	18	1.5	1	90

**Table 3 Required catalyst amount in relation
with configuration improvement**

	13 x 13 cells	15 x 15	17 x 17	20 x 20	21 x 21
p(mm)	9.8	8.0	7.4	6.0	6.0
t(mm)	1.8	1.8	1.4	1.4	1.0
AP(m₂/m₃)	291	321	382	427	470
catalyst Amount Required (%)	100% (Base)	90%	76%	68%	62%

OPERATING EXPERIENCE WITH THE SCR DeNO_x PLANT
IN UNIT 5 OF ALTBACH/DEIZISAU POWER STATION

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ABSTRACT

The SCR DeNO_x plant in Unit 5 (420 MW) of Altbach-Deizisau Power Station has been in operation since late 1985. The plant represents a retrofit to an existing plant and is designed as a partial flow plant (1.1 million m³/h $\approx$ 80 % boiler load).

The experience obtained after 6,000 hours of operation (by the end of 1986) has shown that it is possible to observe the 200 mg NO_x/m³ limit value stipulated in Germany when consideration is given to the accompanying conditions illustrated with full flow plants. The demands placed on the partial flow plant of Unit 5 are particularly high.

The reduction in activity of the catalytic converter is within the expected range after 6,000 hours of operation.

A partial air preheater wash carried out on a test basis produced air preheater water which had a high NH₃ content initially only.

The waste water from the flue gas desulphurization plant contains only a small quantity of NH₃.

The NH₃ values for the flue-dust must be monitored carefully, since they may result in special stipulations being made for operation of the DeNO_x plant.

The maintenance effort for the operational measuring equipment required for the DeNO_x plant is relatively high.

INTRODUCTION - PAST HISTORY

In March 1982, construction work started on the 420 MW unit (Unit 5) of Altbach/Deizisau Power Station. By late 1983, it had transpired that it would be necessary to install a DeNOx plant for this by 1988. After drawing up a feasibility study in spring 1984, the operators, Neckarwerke Elektrizitätsversorgungs-AG, decided to retrofit a DeNOx plant operating according to the SCR principle between the boiler and the air preheater (high-dust system).

In view of the fact that this plant was to be Germany's first large-scale DeNOx plant operating according to the SCR principle, the Federal Environmental Agency (Umweltbundesamt) in Berlin agreed to subsidize construction of the plant.

The manufacturers of the boiler plant, Messrs. L. & C. Steinmueller of Gummersbach, West Germany, were awarded the contract for construction of the DeNOx plant. The conditions accompanying plant installation were as follows:

- Unit startup to schedule, despite installation of the DeNOx plant.
- Installation of the DeNOx plant inside the boilerhouse structure.
- Observance of the expected legal limit value of 200 mg NOx/m³ (NOx; NO calculated as NO₂; referred to 6 % O₂).

THE SCR DeNOx PLANT, UNIT 5

As a result of the above-mentioned accompanying conditions and the progress of construction work by spring 1984, namely

- the flue gas ducts between the boiler outlet and the air preheater had been completed,
 - the air preheater had been installed, its sheet metal covering was ready for installation,
 - the upward draft flue was undergoing production,
 - the entire facade covering for the boiler house was completed,
- only one solution could be found for the DeNOx plant. As compared with the optimum technical solution, this solution necessitated a number of major compromises. This is symptomatic for the upgrading of existing plants.

Figure 1 illustrates the installation situation of the DeNOx plant. The plant is characterized by the following features:

- Partial flow plant: The maximum catalytic converter intake surface and, as a result, the maximum flue gas flow were restricted due to the limited amount of space available. In the case of the DeNOx plant in Unit 5, the entire flue gases (approx. 1.1 million m³/h) are routed via the reactor up to a boiler output of 80 %. When the output is greater, the volume of flue gas exceeding 80 % is routed via reactor bypass ducts at the reactor and added to the main flow (without purification) downstream of the reactor. Figure 2 illustrates the circuit design.
- The reactor is equipped with three catalytic converter and one flow straightening levels.
- In the boiler partial-load range, the minimum temperature required for NH₃ injection (316 °C) is ensured by means of two economizer bypass ducts.
- Installation of the NH₃ dosing unit is only approx. 5 m above the flow rectifiers; the mixing line for distribution of the NH₃ flow is thus extremely short.
- Dampers for closing off the catalytic converters (startup, shutdown, standstill) are located upstream and downstream of the reactor.

- The air preheater was equipped with plates designed specifically for use in DeNOx plants (resistant to dust deposits, easy to clean, enameled central layer, end layer).

A number of technical data are provided in Table 1.

Disassembly of the boilerhouse and the flue gas ducts commenced in June 1984, Figure 1. Installation of the heavy components of the flue gas route was able to be completed by November 1984. By the time winter started, the boilerhouse was able to be closed again. Power generation in the block commenced on schedule in summer 1985. The catalytic converters were installed in November 1985 during a ten-day shutdown period. December 1985 saw NH₃ dosing for the first time; operation of the DeNOx plant thus commenced.

The NH₃ required for operation of the DeNOx plant is stored in liquid form in two partially buried 120 m³ tanks. With this storage method, the tank heads project into the storage building, Figure 3. The NH₃ is supplied in railroad tank cars. The discharging units and the NH₃ evaporators are housed in the machine room. The gaseous NH₃ provided after processing in the evaporator station is mixed with air and added to the flue gas.

The control diagram of the DeNOx plant is shown in Figure 4. The NH₃ dosing volume is specified by means of a control operation by multiplying the load signal by the difference resulting from the NOx content upstream of the reactor and the emission reference value (200 mg/m³). NH₃ dosing is corrected on the basis of the NOx value upstream of the air preheater as a function of comparison of the actual and the reference value. Due to the fact that NH₃ measuring equipment was not available, control of the NH₃ concentration downstream of the catalytic converter (NH₃ leakage) as planned originally was not implemented as a further superordinate control variable for NH₃ dosing. The temperature regulation system controls the dampers in the startup and partial load range.

COST SITUATION

A cost framework totalling DM 65 million was calculated for the entire DeNOx plant retrofit project. The specific costs are in the region of approx. DM 150.00/kW. This value is within the cost framework for existing plants which can be retrofitted with the minimum of cost. The total capital cost for the plant (incl. DeNOx plant) was almost DM 900 million.

OPERATING EXPERIENCE

MEASURING SYSTEMS

Figure 5 illustrates the measuring points installed for operation of the DeNOx plant. Gas is tapped on two measuring levels upstream and downstream of the catalytic converter in a net-like manner at 12 points on the flue gas duct cross-section respectively. All gas tapping points are designed as bypass lines through which large volumes of gas flow with the assistance of blowers. All flue gas pipes are equipped with electric backup heaters (150 - 200 °C and 250 °C). For the purpose of NO measurement downstream of the catalytic converter, gas tapping includes a gas treatment process which selectively removes NH₃ from the measuring gas flow. This prevents the measuring gas lines and the measuring device from being contaminated as a result of the formation of ammonia salts. All measuring devices are housed together in a fully air-conditioned measuring room. The maintenance effort for the operational measuring equipment is considerable.

A variety of measuring devices are employed during timed measuring campaigns in order to carry out constant measurement of the NH_3 content. Reliable and reproducible results have been obtained using a device provided by the Fraunhofer Institute for Physical Measuring Technology in Freiburg. The device employs a diode laser spectrometer.

Particularly high demands are placed on measuring gas treatment for NH_3 measurements (2,3). Special consideration must be given to heating (350°C), the choice of material (titanium piping) and the dwell time of the flue gas in the sampling system (2).

Special absorption curves were selected for the diode laser (3) in order to eliminate cross-sensitivities (CO , H_2O).

Further items of measuring equipment operating according to the infra-red absorption measuring principle (4) and a catalytic reaction of NH_3 and NO by means of the chemoluminescence principle (5) were unable to be employed in a manner offering adequate safety in the low concentration range found here ($\approx 1 \text{ ppm NH}_3$).

For the purpose of continuous NH_3 measurement, the experience obtained to date indicates that the expenditure and maintenance effort for the equipment employed greatly exceeds the level to which the equipment normally found in power stations is subjected.

For this reason, wet chemical NH_3 analysis methods which determine the NH_3 content by means of photometry were employed during special measuring campaigns in order to carry out detailed checks into catalytic converter behavior (6). Although these measurements are elaborate, they can be carried out with a high level of versatility and are capable of providing specific information on the NH_3 concentration downstream of the catalytic converter over the entire duct cross-section (viz. NO_x Separation below).

Similarly, the NO concentration upstream and downstream of the catalytic converter was measured during the measuring campaigns using mobile measuring probes (viz. NO_x Separation below).

STARTUP AND SHUTDOWN BEHAVIOR, STANDSTILL BEHAVIOR

As a medium-load plant, Unit 5 is shut down daily in the summer months and over the weekend in the winter months. No restrictions as regards the operation method have resulted due to the operating requirements of the De NO_x plant (1). The only factor restricting catalytic converter operation is observance of the minimum temperature of 316°C for NH_3 injection. Figure 6 illustrates a startup operation in the form of a diagram. Special insulating measures ensure that the cool-down rate of the catalytic converter when the dampers are closed for weekend standstill periods is maintained at a sufficiently low level (0.6°K/h), thus eliminating the need for special heat retention measures for the catalytic converter (e.g. heating system).

The startup time for Unit 5 is approx. 30 minutes after an overnight standstill and approx. 45-60 minutes after a weekend standstill period.

NO_x SEPARATION

General Remarks

In accordance with the generally accepted reaction equations for SCR technology, it must be ensured that the NO mass flow equates exactly with the corres-

ponding NH_3 mass flow both as regard its size (desired overall mol ratio) and location. Parameters which influence or impair solution of this problem in large-scale plants include

- the velocity curve upstream of NH_3 dosing,
- the NO_x concentration curve upstream of NH_3 dosing, and
- NH_3 dosing
- the mixing process between flue gas and NH_3 .

Deviations from the ideal state naturally occur as a result of an unavoidable fluctuation amplitude under technical operating conditions and due to irregularities over the flue gas cross-section (curves).

For example, tolerance ranges for the intake parameters are assumed:

NO_x intake concentration mg/m^3	600	600
NO_x discharge concentration mg/m^3	200	100
Separation level	66 %	83 %
Unequal distribution, NO_x concentration		+ 5 %
Unequal distribution, flue gas velocity		+ 10 %
Unequal distribution, NH_3 dosing		+ 10 %

Using these assumed values, extremely close tolerance ranges were selected for large-scale plants.

The left-hand side of Figure 7 illustrates that an extremely high NO_x discharge concentration can result for the intake concentrations when the least favorable tolerance combination for NO_x separation is superimposed (NO_x plus tolerance, velocity plus tolerance, NH_3 minus tolerance). In the other extreme instance of tolerance combination (NO_x minus tolerance, velocity minus tolerance, NH_3 plus tolerance), the NO_x concentration at the outlet can theoretically be less than 0 in the case of a discharge concentration of $100 \text{ mg NO}_x/\text{m}^3$ (right-hand column), i.e. NH_3 is still present without having NO_x as a reactive partner (from Point A). This results in NH_3 leakage, even under ideal mixing and reaction conditions.

Under realistic conditions, the area indicated results for the NO_x content at the outlet. Observance of the requested NO_x limit value (average) can be achieved by increasing NH_3 dosing slightly (equal areas in the 3rd diagram; thin line). An increase in NH_3 leakage is accepted (ideal curve A'). A qualitative indication of NH_3 leakage is provided in the lower section of the diagrams. It must be noted that for a discharge concentration of $100 \text{ mg NO}_x/\text{m}^3$ (right-hand column) not even a larger catalytic converter is capable of altering these conditions to a major extent. The example provided indicates that even at a separation level of 80 %, problems such as those described above can occur as a result of unequal distribution. When stipulating the limit values, these "technical deficiencies" must be taken into consideration.

In the description of Unit 5 provided earlier in this paper, it was shown that the De NO_x plant installed here is a so-called partial flow plant. The separation levels required for full-load operation of this plant (80 % flue gas volume through the catalytic converter; 20 % reactor bypass flow) are illustrated in Figure 8 as a function of the NO_x intake concentration. By way of comparison, a full flow plant was also included (100 % flue gas = 100 % catalytic converter design). The figure indicates that the above-mentioned 80 % separation level limit for partial flow plants is achieved relatively quickly. For this reason, special consideration must be given to achieving lower NO_x intake concentrations (primary measures), in addition to optimizing the intake parameters.

Measurement Results, Unit 5

These fundamental considerations were able to be indicated clearly on the basis of test series carried out on the DeNO_x plant in Unit 5.

Tests carried out in the wind tunnel and the installation of additional flow baffles enabled the flow curve to be homogenized upstream of the catalytic converter (1,2).

Figure 9 illustrates a NO_x curve above the flue gas duct cross-section upstream of NH₃ injection. With a standard deviation of only 2 %, it is well-compensated.

First measurements of the NO_x curve downstream of the catalytic converter showed marked deviations. Trimming of the 20 NH₃ injection lances represented an initial attempt to homogenize NO_x concentration distribution. The result of this initial measure is indicated in Figure 10. The standard deviation is 80 mg NO_x/m³. This value would be acceptable for full flow plants in certain cases, but not for the partial flow plant in Unit 5 since the mean value downstream of the catalytic converter for an intake concentration of 600 mg NO_x/m³ must be 100 mg NO_x/m³ and not 230 mg NO_x/m³ as shown in Figure 10 (viz. Figure 8).

It was not possible to improve the NO_x curve by means of further trimming of NH₃ injection, and so it was necessary to make fundamental alterations to the NH₃ injection system for the purpose of improving mixing. The following figures illustrate the results following alteration of the injection system. Figure 11 shows the course of the NO_x curve downstream of the catalytic converter.

The reactor was operated with a stoichiometric NH₃/NO_x ratio of 0.59. The separation value was slightly less than 59 %. The NO_x discharge value calculated over the cross-section was approx. 230 mg NO_x/m³. As compared with Figure 10, the marked reduction in the standard deviation of 80 mg NO_x/m³ to 37 mg NO_x/m³ is particularly noticeable. The progress made as a result of improving the NH₃ injection system is thus obvious.

NH₃ leakage measurements carried out on 7 tie-bars parallel to this resulted in a leakage of approx. 0.3 mg NH₃/m³ over the flue gas duct cross-section (Figure 12). Although the NO_x curve still indicates a certain amount of unbalance in a number of cases, it was able to be accepted in view of the low leakage value.

Figure 13 illustrates the NO_x curve downstream of the catalytic converter for almost identical intake conditions when operating the plant with a stoichiometric factor of 0.85. The mean NO_x value downstream of the catalytic converter is approx. 100 mg NO_x/m³. With an intake concentration of 600 mg NO_x/m³, this corresponds to 200 mg/m³ operation for the Unit 5 partial flow plant at full boiler load. With 39 mg NO_x/m³, the absolute standard deviation value is similar to that obtained in the preceding test. However, the percentage deviation is almost twice as great since the reference value is correspondingly lower.

NH₃ leakage measurements conducted parallel to this are illustrated in Figure 14. The pronounced inhomogeneity of the NO_x curve shown in Figure 13 with the very low NO_x values at K 12 is seen in the marked increase in leakage along the groove at measuring point K 12. This fact clearly confirms the risks which can result due to velocity curves, unequal distributions in the NO_x intake curve and due to non-homogeneous NH₃ addition at a high separation level. Trials are currently being carried out to reduce NH₃ leakage even further by lowering the NO_x intake concentration, making further improvements at the NH₃ injection stage and by improving mixing.

The results presented in Figures 10-14 indicate the design of the measures required to measure NH_3 leakage and the equipment best suited for use (2).

DYNAMIC BEHAVIOR

In Figure 15, the following curves are drawn over the time axis:
NOx upstream of catalytic converter - NOx downstream of catalytic converter - NH_3 dosing - Boiler load.

In particular, this diagram illustrates the NH_3 emission process from the catalytic converter when NH_3 dosing is reduced. The delay in NOx reduction when further NH_3 is added is lower, although it can still be clearly seen. Dynamic aspects of the measuring system are included in these transition functions.

Figure 16 illustrates the behavior of the plant when the load is changed over a period of time. The following curves were drawn:

NOx upstream of catalytic converter - NOx downstream of catalytic converter - NOx upstream of air preheater - NH_3 dosing - Stoichiometric factor - Boiler load.

The "NOx downstream of catalytic converter" and "NOx upstream of air preheater" curves are identical up to a boiler load of approx. 80 % (reactor bypass closed) and, as the boiler load increases, diverge in accordance with the opening of the bypass dampers (partial flow plant). The reference value for this trial was 180 mg NOx/m³.

Figure 17 illustrates half-hourly values for the plant over the course of one day. The regulation system employed (Figure 4) is capable of maintaining the plant at the prescribed limit value.

Today, the DeNOx plant in Unit 5 can be operated in such a way as to reliably ensure that the 200 mg NOx/m³ limit value is observed up to a boiler load of 80 %.

Optimization work is still required for the load range greater than 80 %. This work is related to the high demands of the partial flow plant installed in Unit 5.

CATALYTIC CONVERTER BEHAVIOR

The change in catalytic converter behavior as regards initial behavior was examined after 1,480; 3,600 and 6,000 hours of operation. The results of the examinations are provided in Figure 18. The activity loss (lower curve) on which design was based was also included. It can be seen that the drop in activity is within the expected range.

In addition to the laboratory measurements conducted, the catalytic converter was inspected several times and subjected to visual examinations in order to detect any blockages or traces of erosion. Figure 19 on the left illustrates the intake side of the catalytic converter. No signs of wear or blockages of the catalytic converter ducts are visible. Even after 6,000 hours of operation, the catalytic converter is still in an excellent condition. The blurred grate-like structure in the illustration is the outline of the wire net placed in front of the catalytic converter to protect it against large agglomerations of dust. Filigree dust deposits can be seen on the discharge side; when these are released, however, they disintegrate or are crushed on the wire net upstream of the next catalytic converter stage, thus preventing damage.

AIR PREHEATER LONG-TERM BEHAVIOR

In the case of SCR plant operation directly downstream of the boiler (high-dust system), the question of what happens to NH_3 leakage was discussed.

Literature on the subject (7) hints that NH_3 leakage is probably divided up, with 10 % being deposited in the air preheater, 60-70 % being deposited on the dust (discharge via the E filter), 10 % as flue gas desulphurization plant waste water and 10 % emission via the chimney.

Both the NH_3 content on the flue-dust and the NH_3 content in the flue gas desulphurization plant waste water can (with some effort) be recorded to a certain extent (in a close-knit temporal sequence). The deposits in the air preheater were not included in this "continuous" observation. Investigations here must be restricted to periods in which the plant is at a standstill.

In December 1986, after approx. 8,000 boiler operating hours and approx. 5,500 DeNOx plant and NH_3 injection operating hours, the air preheater underwent detailed examination. A major change in the pressure drop at the air preheater during operation was not yet detected. Visual inspection of the air preheater plates showed only minute deposits at the faces, and the overall assessment was extremely positive.

The Rothemuehle air preheater system (fixed sheet packages, rotating hoods) is equipped with "DeNOx-tailored sheets" (easy-to-clean, deposit-resistant sections, central and end layers enameled). The air preheater is blown through daily as part of routine power station operations.

In order to investigate the very uncertain statements as regards the consequences of NH_3 leakage in the air preheater and the consequences of an air preheater wash which may become necessary (water volume, materials contained), one segment of the air preheater was washed in December 1986, Figure 20. The large-scale washing process was simulated for the test wash. To do this, a segment of the heat exchanger was washed with the proposed amount of water in the cycle of the proposed air preheater wash using high-pressure water. The washing water for each washing cycle was collected and analyzed.

Figure 21 indicates the results of the analysis for the pH value and the NH_3 content of the individual washing cycles.

The washing water quantity was approx. 110-120 l/washing cycle, thus resulting in a specific value of approx. 0.5 l/m² and washing cycle.

The estimate for the entire air preheater of Unit 5 results in a need for approx. 50 m³ per cycle. This results in approx. 500 m³ of washing water for the entire air preheater in order to achieve the purity level (10 cycles) attained in the trials. The relatively rapid wash-out of easily soluble ammonia salts can be clearly seen (Figure 21).

In view of the disposal of the air preheater washing water, it seems advisable to divide the washing water into certain doses (e.g. wash 1-5: average NH_3 content 130 mg/l; COD 320 mg O₂/l; removable substances 15 ml/l; wash 6-10: average NH_3 content 12 mg/l; COD 92 mg O₂/l). If further washing operations are required, these do not differ greatly from "conventional" air preheater washes carried out in the past.

Following test washing, the washed air preheater packages were drawn and indicated a very clean, bright surface.

The estimate of the amount of NH_3 washed out results in approx. 30 kg for the entire amount of NH_3 deposited on the air preheater as a whole. The attempt to estimate the total operating time results in a deposit rate of approx. 1 % of the NH_3 leakage in the air preheater. In view of this fact, consideration must be given to the low NH_3 leakage which prevailed in the past and to DeNOx-specific metal covering with daily blow-through.

FLUE GAS DESULPHURIZATION PLANT WASTE WATER

A flue gas desulphurization plant operating according to the Knauf Research-Cottrell principle (limestone washing process) is installed in Unit 5. The waste water from the flue gas desulphurization plant is treated in a 2-stage waste water treatment plant by raising the pH value to approx. 9.0. The average waste water values are between 5 and 6 ppm NH_3 , and maximum values between 8 and 9 ppm NH_3 . The values correspond well to the results of measurements conducted on other plants (8). Thus, it is possible to observe the limit values applicable in Germany for direct discharge of the waste water into the receiving water (< 10 ppm NH_3).

DUST LOADING

The NH_3 concentration in the flue-dust is recorded as part of operating data measurement. The dust content of the flue gases is between 6 and 7 g/m³.

The NH_3 content in the flue-dust is subject to major fluctuations, on average 20-50 mg NH_3 /kg. These values indicate that questions concerning NH_3 deposits on the flue-dust will become more significant in future with regard to the use of fly ash, and that these will have a decisive influence on the demands placed on operation of DeNOx plants and the warranty values to be observed.

Using the results obtained with regard to dust concentration, air preheater deposits and flue gas desulphurization plant waste water loading, an attempt was made to make conclusive statements. No satisfactory convergence was able to be achieved. Deviations were between 20 and 30 %. Literature on the subject (8) provides information on deposits in the flue gas section of the air preheater and on direct, subsequent emission of these NH_3 deposits in the air section of the air preheater together with the combustion air and the subsequent thermal decomposition in the firing chamber. NH_3 leakage volumes of 25 - 35 % are stated for this.

SUMMARY

A considerable amount of effort went into installing the DeNOx plant in Unit 5 of Altbach/Deizisau Power Station which was under construction in 1984. Due to the fact that this represents a retrofit to an existing plant, certain compromises had to be made with regard to the optimum plant configuration (partial flow plant). By the end of 1986, the DeNOx plant had been in operation for approx. 6,000 hours.

The operational experience gained indicates that, in principle, observance of the 200 mg NO_x /m³ limit value is possible for full flow DeNOx plants with corresponding NO_x intake concentrations (primary measures < 600 mg NO_x /m³). Special consideration must be given to uniform velocity distribution and a good NH_3 mix. These requirements are more stringent for partial flow plants.

The maintenance effort for the operational measuring equipment for NO and O_2 is extremely high. Continuous measurement of NH_3 leakage with the maintenance effort normally required for such plants or by means of sensible resolution of the measured values for the NH_3 leakage values commonly found today is not yet possible.

After 6,000 hours of operation, the drop in activity of the catalytic converter is within the expected range.

A first (and, from the point of view of the operating condition, not yet necessary) partial air preheater wash resulted in air preheater washing water which

only showed a high NH_3 content initially. The NH_3 deposits in the air preheater were low. The waste water from the water treatment system of the flue gas desulfurization plant has only a minor NH_3 content ($< 10 \text{ mg/NH}_3/\text{l}$).

The question of NH_3 deposits on the flue-dust will gain in significance in the years to come and, in certain cases, will have a major influence on operation of the DeNOx plant.

The information provided applies for a DeNOx plant operating period of approx. 6,000 hours. A close watch will be kept on further developments.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

ACKNOWLEDGMENTS

The results presented here are based on numerous measurements in which a large number of staff were involved. For this reason, I would like to conclude by expressing my thanks to the staff of the plant supplier and to the institutes involved in taking the measurements, as well as to the staff of the power station, the laboratory and of our company headquarters for their valuable assistance.

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TABLE 1. TECHNICAL DATA

DeNOx Plant of Altbach/Deizisau Power Station, Unit 5

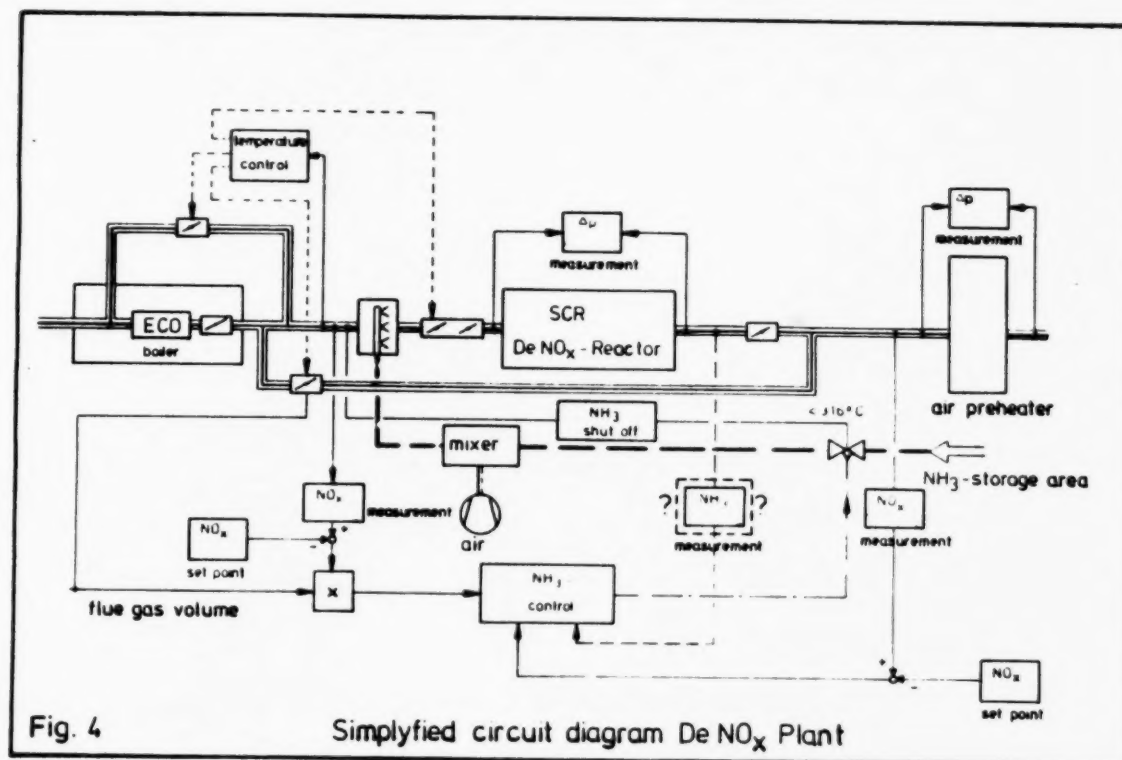
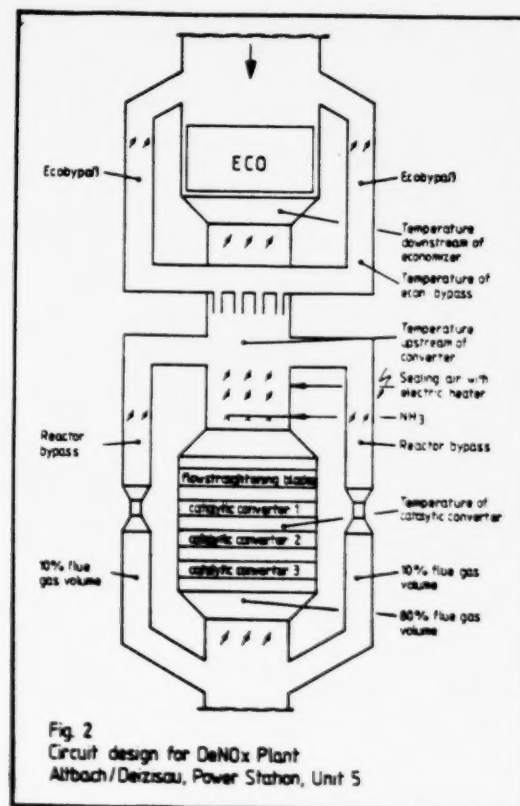
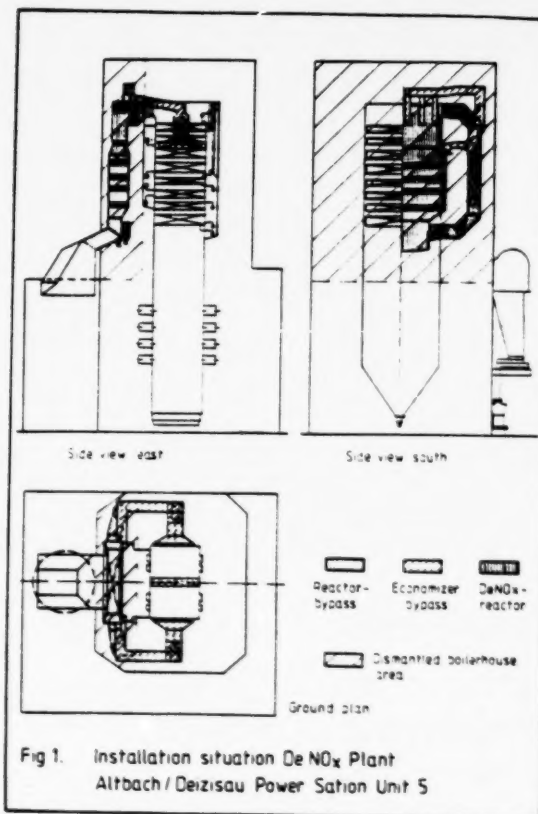
Plant supplier:	Messrs. L. & C. Steinmueller GmbH, Gummersbach
Design volume flow rate	1,039 million m ³ /h
Catalytic converter volume	311 m ³
Catalytic converter weight	217 t
Space velocity	3,340 h ⁻¹
Catalytic converter type:	titanium-dioxide-based
	Va - Wo - Type
Catalytic converter element	100 x 15 x 15 cm
Honeycomb size	7.5 mm
Wall thickness	1.4 mm
Catalytic converter baskets	216 baskets with 8 x 8 elements

Air Preheater Plant

Rothemuehle System

Fixed heat exchanger packages, rotating hoods

3 layers of DeNOx-tailored sections	Hot-end layer
	Central layer, enamelled
	End layer, enamelled



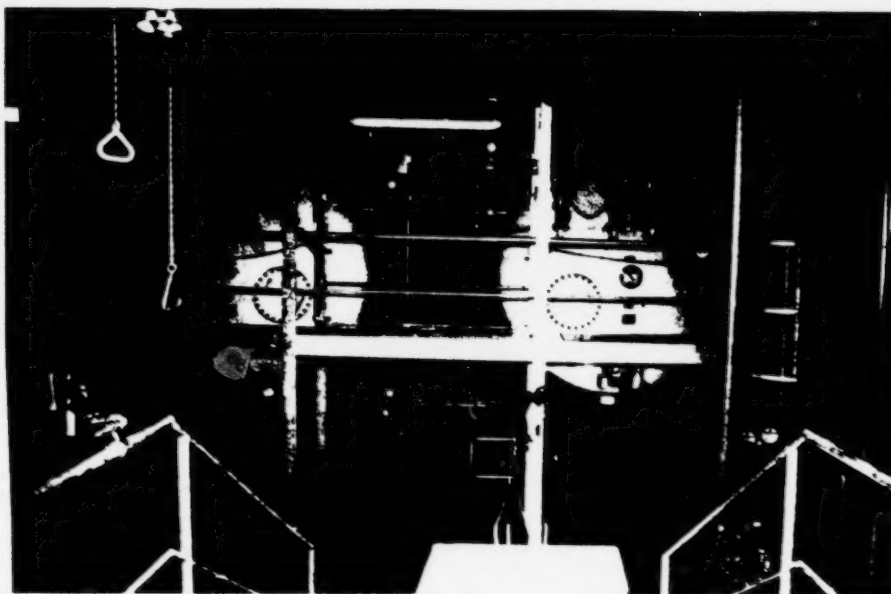


Fig. 3

NH₃ storage area

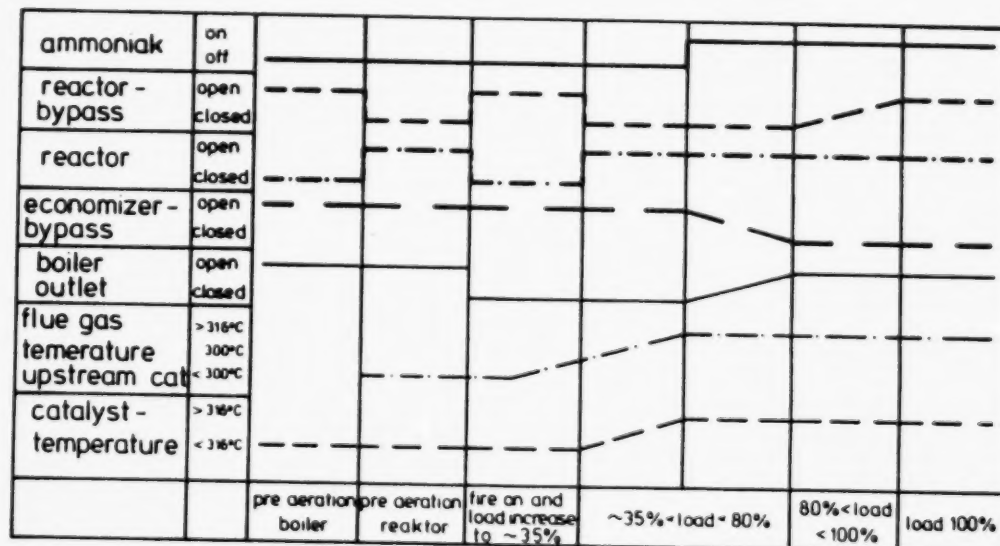
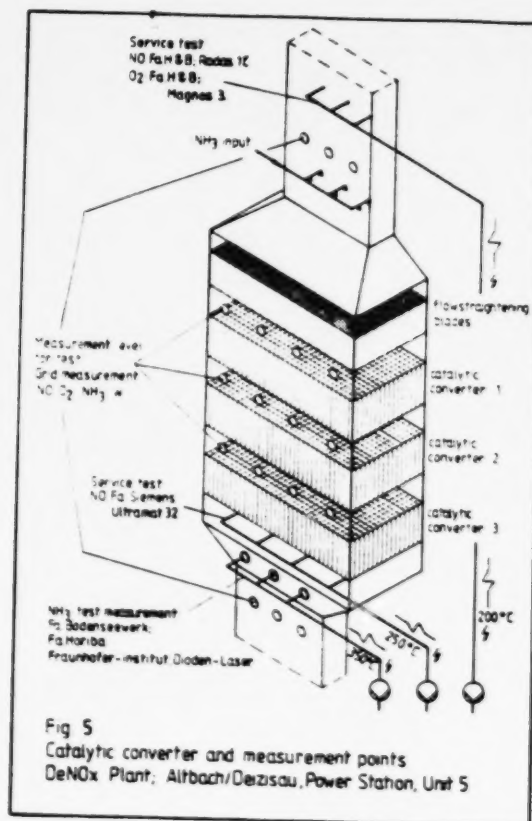


Fig. 6

Start up diagram

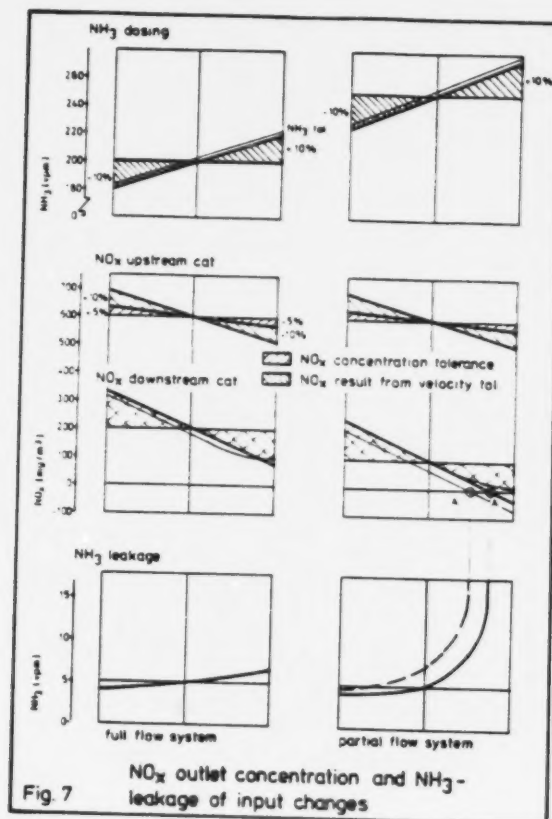


Fig. 7 NO_x outlet concentration and NH_3 -leakage of input changes

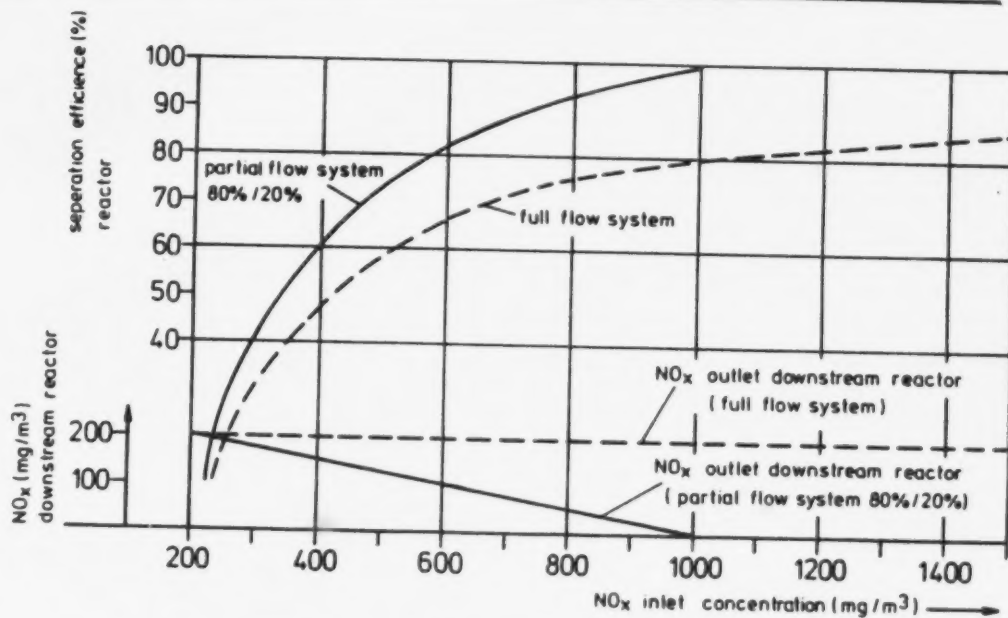


Fig. 8

Separation efficiency by NO_x outlet concentration 200mg/m³ partial flow system / full flow system

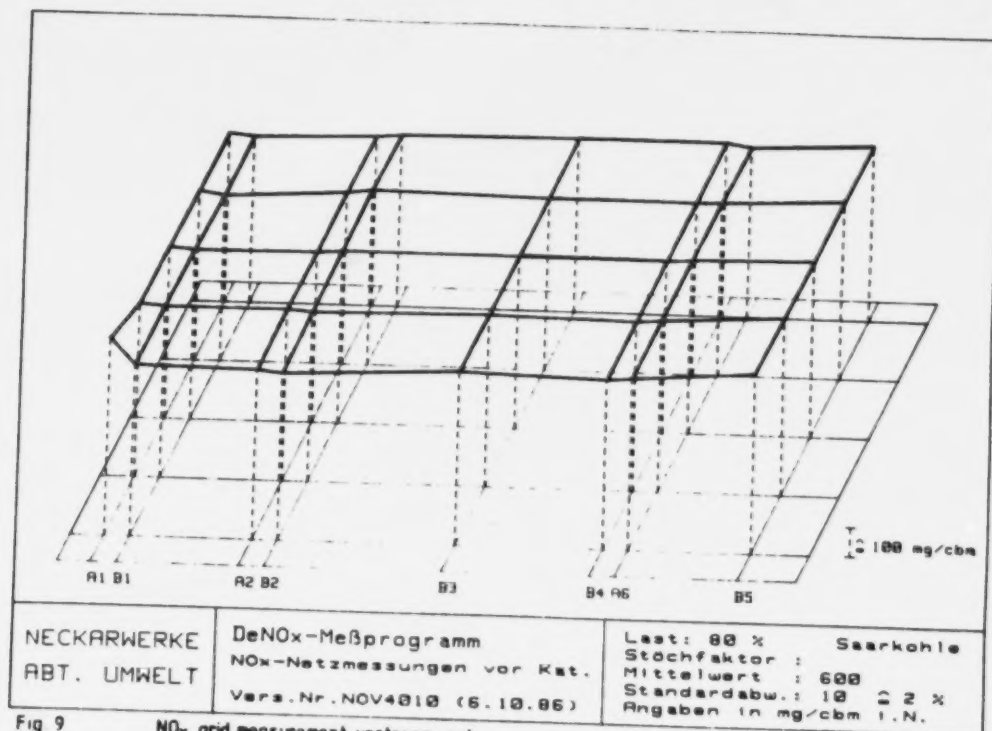


Fig. 9 NO_x grid measurement upstream cat

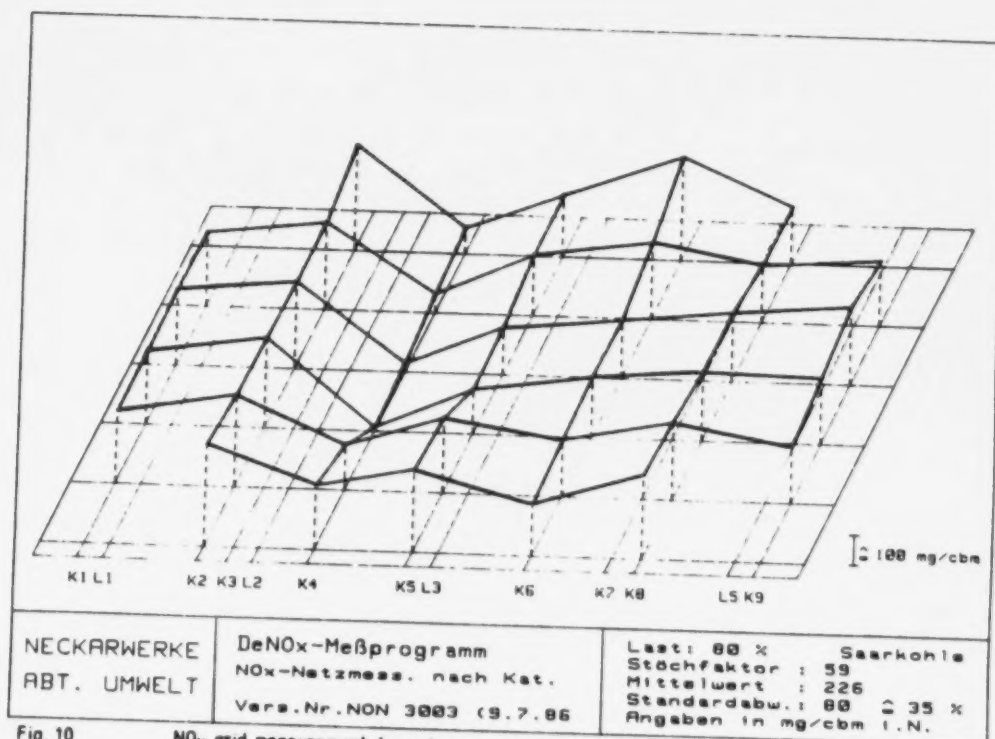


Fig. 10 NO_x grid measurement downstream cat

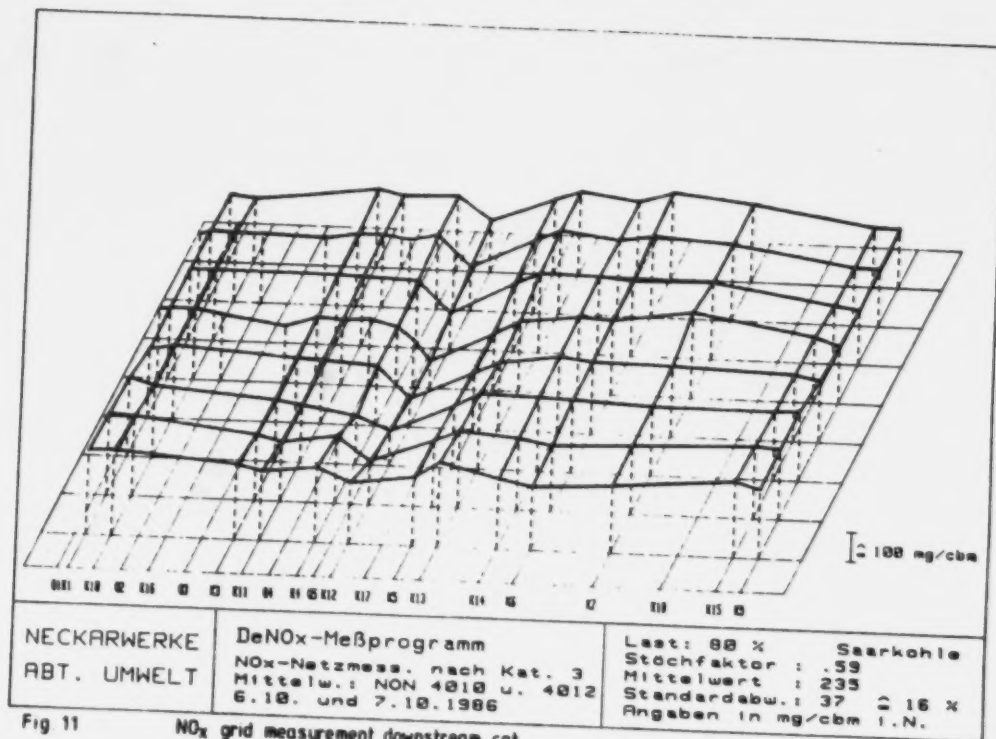


Fig 11 NO_x grid measurement downstream cat

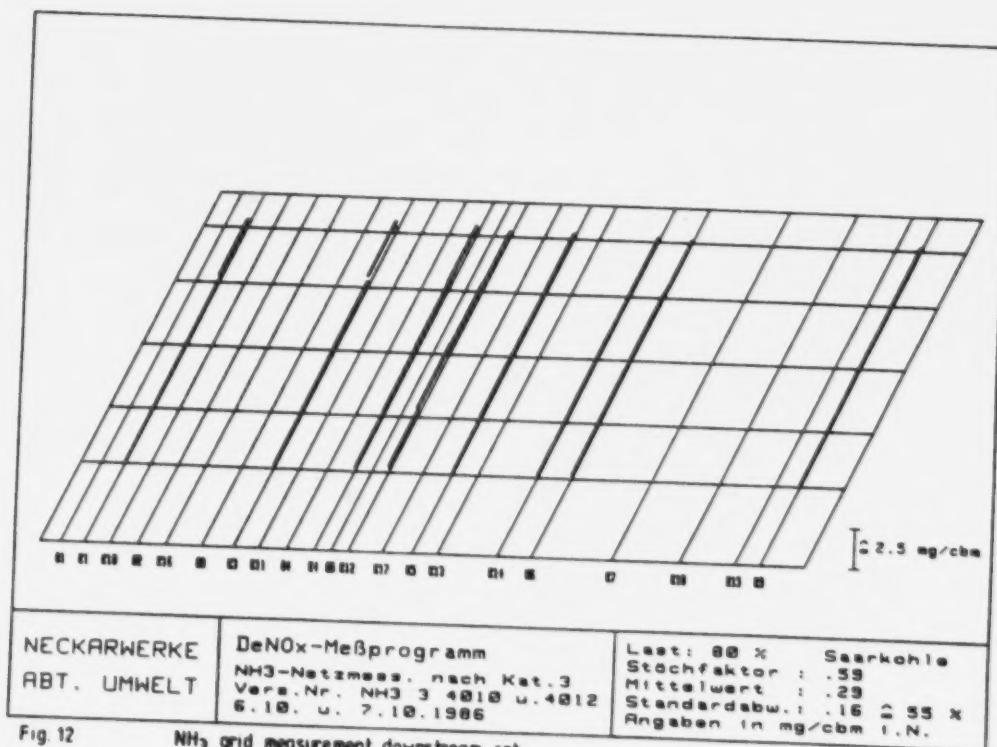


Fig. 12 NH₃ grid measurement downstream cat

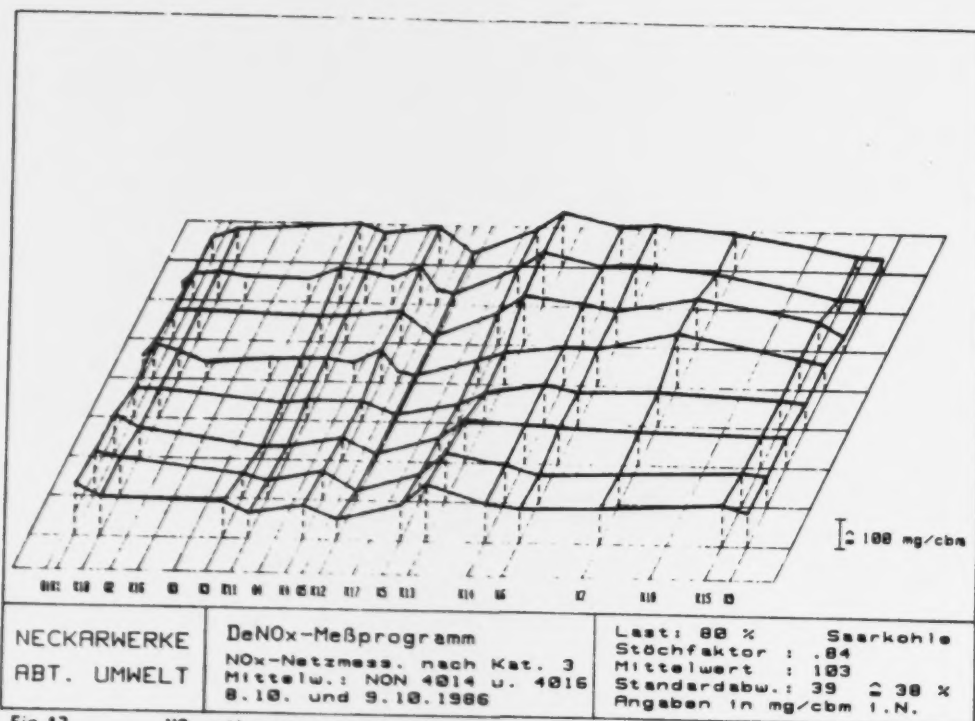


Fig. 13 NO_x grid measurement downstream cat

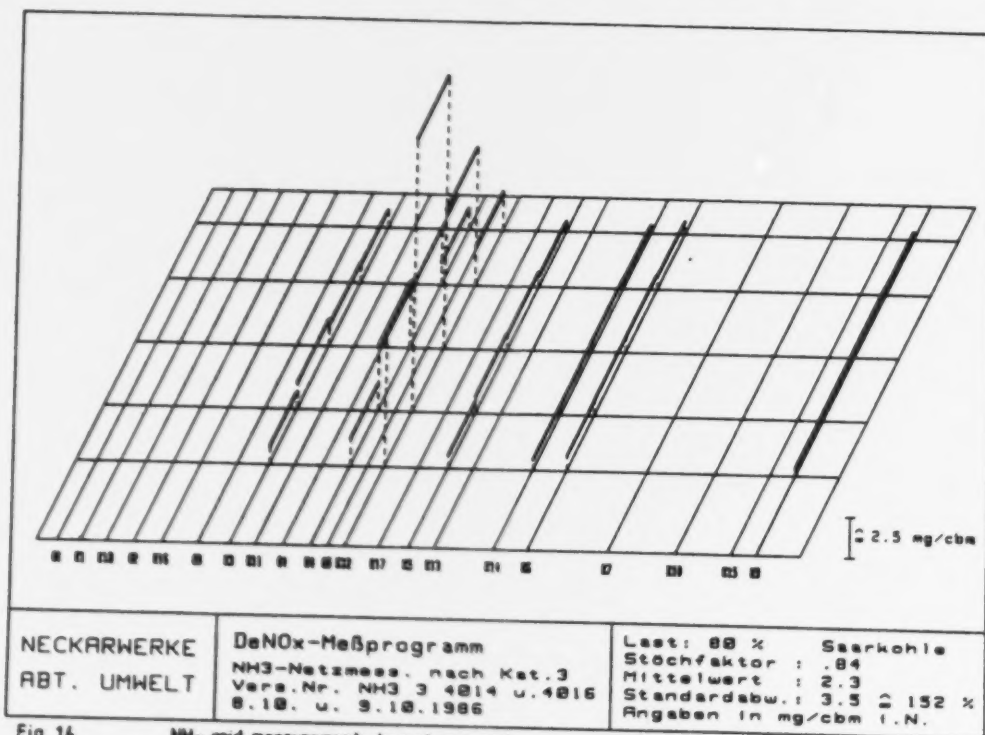


Fig. 14 NH₃ grid measurement downstream cat

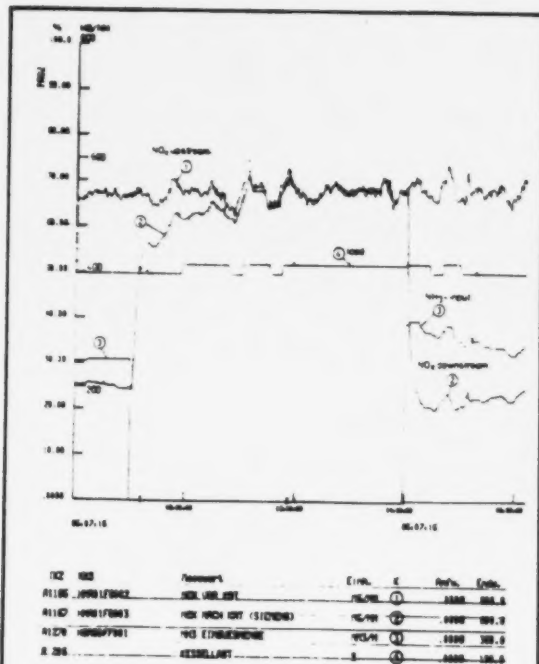


Fig. 15 NO_x concentration downstream of catalytic converter by changing NH₃-input

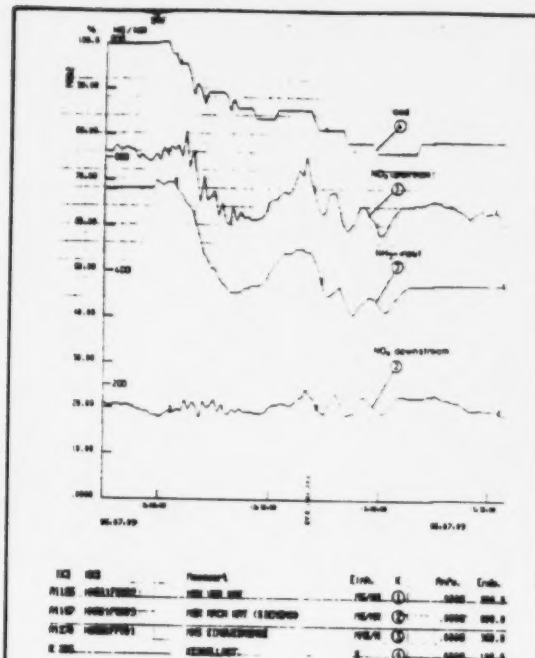


Fig. 16 NO_x concentration downstream of catalytic converter by changing load

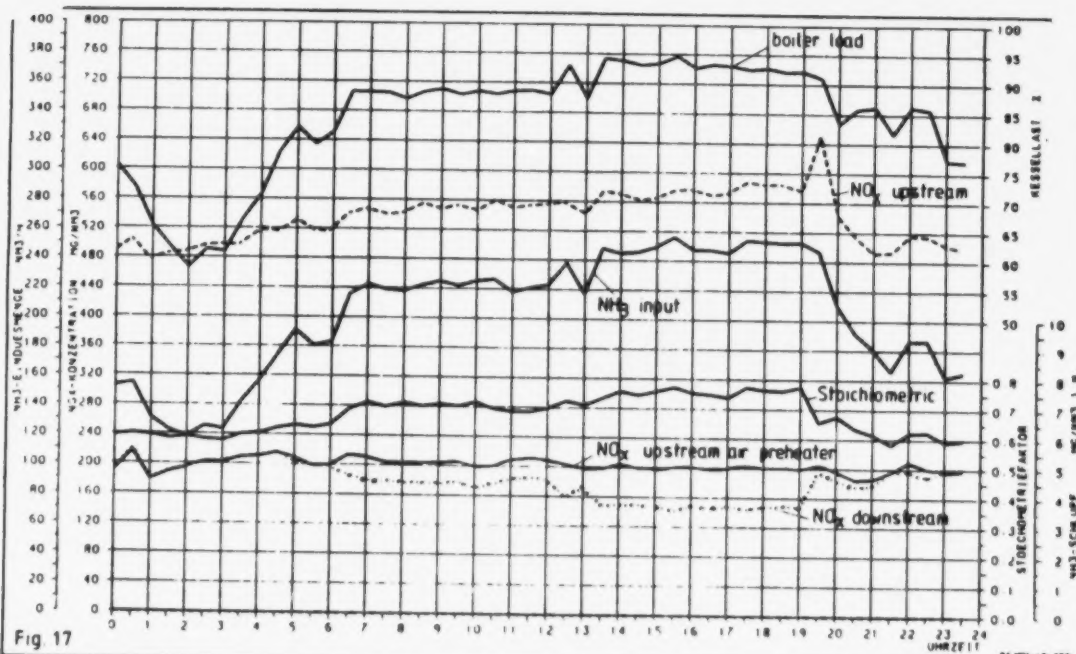
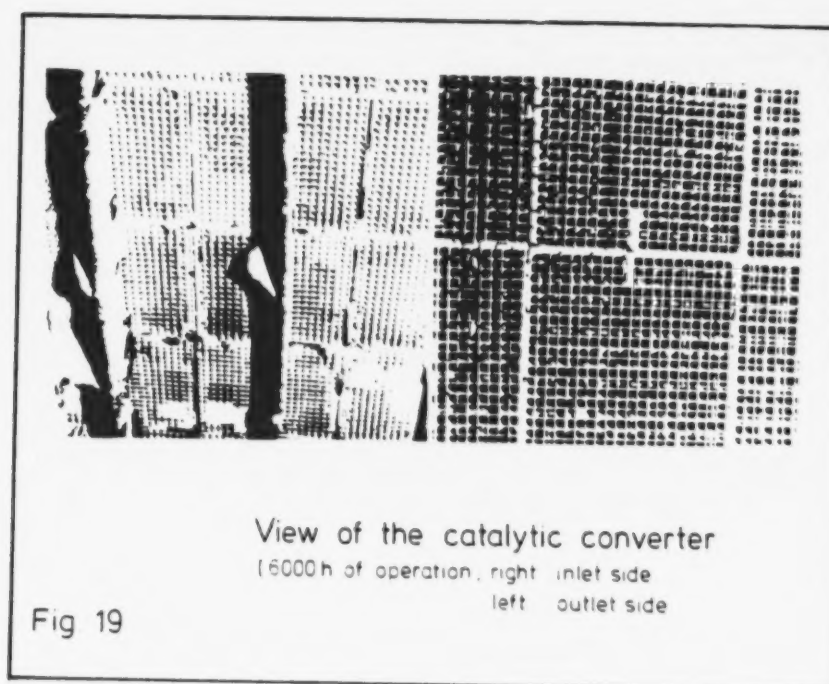
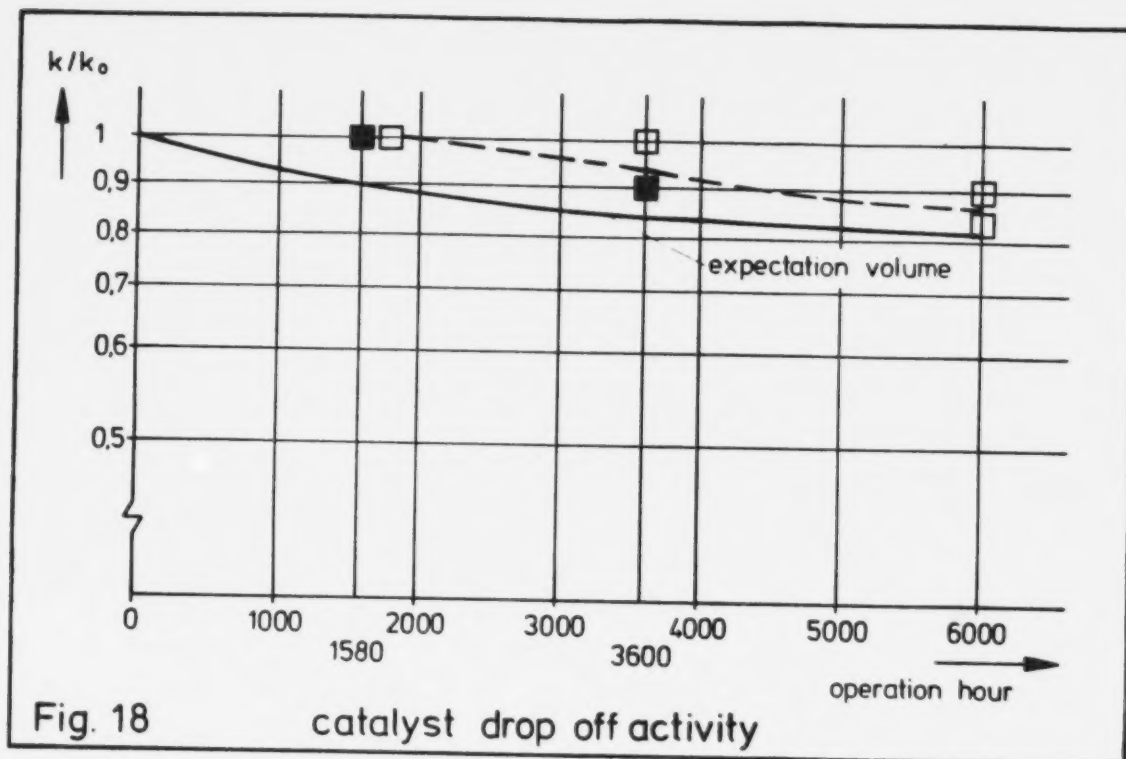


Fig. 17

NECKARWERKE
FABRIK FÜR KRAFTWERKE
ABTEILUNG UMWELT

KRAFTWERK ALTACH DEUTSCHLAND
DENOX-ANLAGE BLOCK 5
•• 26.01.87 ••

■ KESSELASPE
■ NH3 VOR KATALYSATOR
■ NH3 NACH KATALYSATOR
■ NH3 VOR LUFT
■ NH3 FÜR DIE ANLAGE
■ STÖCHIOMETRIEFaktor
■ NH3-SCHLUPF



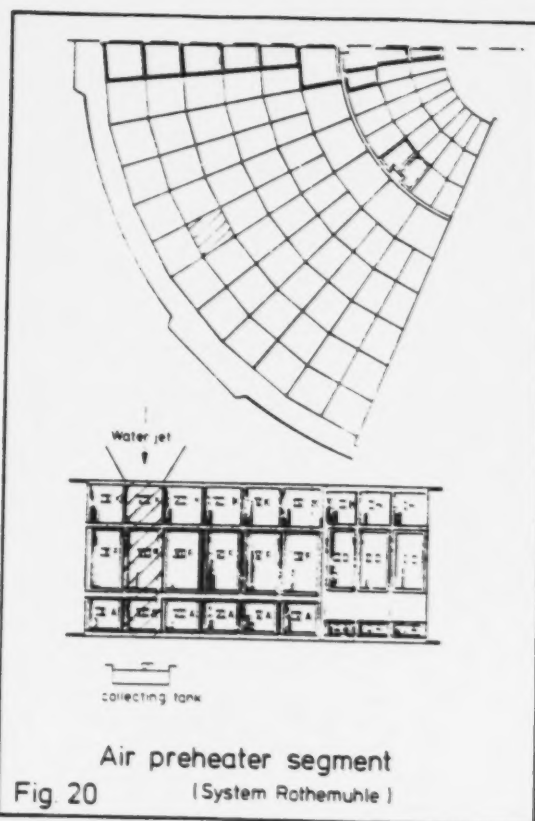


Fig 20

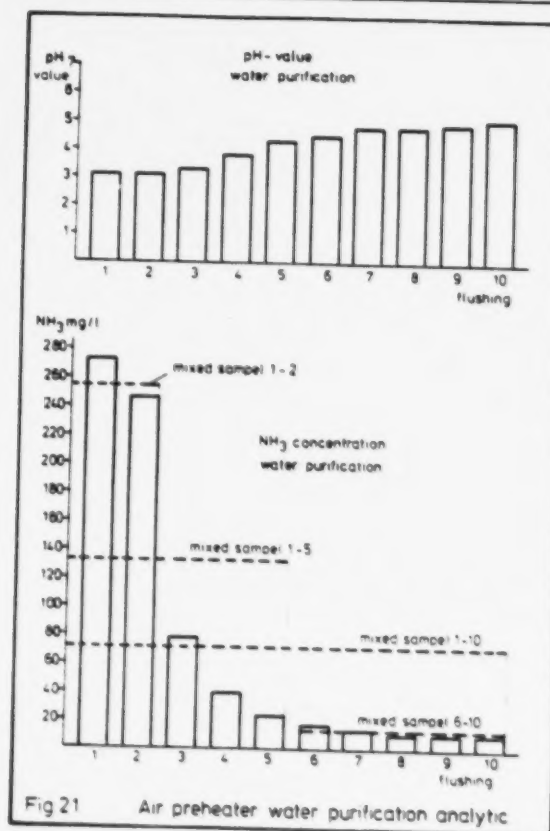


Fig 21

Air preheater water purification analytic

VKR FULL-SCALE SCR EXPERIENCE
ON HARDCOAL FIRED BOILERS

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ABSTRACT

VEBA Kraftwerke Ruhr (VKR) operates powerplants in Northrhine-Westfalia of the Federal Republic of Germany with a total capacity of 5500 MW gross. Most of the boilers are fired with high ballast hardcoal. Older boilers have wet bottom furnace, newer one's are dry furnace type. The great furnace ordinance of Germany calls for a NO_x emission rate 200 mg/m³, i.e. 98 ppm, so all great boilers must be retrofitted by DENOX systems.

Meanwhile VKR reduced NO_x emission from their boilers by primary methods as far as possible. Since end of 1984 VKR handles up to 8 pilot-plants to prove the SCR technology. Since end of 1985 100 % of fluegas from district heating boiler Buer (dry bottom, 150 MW) and since mid 1986, sponsored by UBA, 50 % of fluegas from boiler Knepper C (molten ash, 370 MW) are treated by SCR high dust technology.

Basing on pilotplant-tests the paper describes both DENOX demonstration units, their operation and the obtained findings.

INTRODUCTION

VEBA Kraftwerke Ruhr (VKR) operates at 9 stations in Northrhine-Westfalia of the Federal Republic of Germany powerplants with the total capacity of 5500 MW gross. The main part, namely 28 boilers, are fired with pulverized hardcoal of the Ruhrdistrict, whereby high ballast coal predominates. The older 19 boilers have wet bottom furnaces and the 9 newer plants are equipped with dry bottom furnaces, see figure 1.

On occasion of performance of the 13. Ordinance Implementing the Federal Immission Control Law, the so-called "Ordinance of Large Firing Installations", all coalfired large boilerplants will be retrofitted with FGD latest until mid 1988, because meanwhile for this technic know-how is present by the FGD units operating with new boilerplants.

To reduce NO_x emissions by secondary methods it is necessary to adapt the technology, which is mainly descended from Japan, to the German operation conditions. These are:

- Burning high ash coal with higher sulfur content,
- high NO_x concentrations at the rawgas side,
- operation of wet bottom furnaces with and without flyash-recycling, an unknown technique in Japan and
- boileroperation at midload conditions with clear oscillations of the load factor, partially with daily start up and turn off as well as standby at weekends.

To reduce the rawgas NO_x concentration VKR has meanwhile realized primary methods at most of their coalfired boilers.

Additionally since the end of 1984 VKR operates 8 SCR pilotplants downstream different boiler furnaces.

At the end of 1985 the SCR demonstration unit on the high dust side of the coalfired dry bottom boiler of FWK Buer was started, followed by an Exxon unit at the district heating boiler in Marl in February 1986. In June 1986 the tests started with the demonstration plant of the boiler Knepper C. All 3 boilers are fired with ballast coal, whereby the boilers at Marl and Knepper are of the wet bottom type.

VKR believes that for oilfired boilers the SCR technique can be taken over direct from Japan. Therefore one of both 714 MW oilfired boilers at powerstation Scholven is retrofitted with a SCR unit since October 1986. The second boiler get this SCR plant till autumn 1987.

Including the required tests of the new technology as well in pilot- as also in large testunits the coalfired large boilerplants of VKR will be retrofitted with DENOX systems at about 1989/1990 to observe the NO_x emission limit of 98 ppm (gasside), corresponding to 200 mg/m³, recommended by the conference of the ministers for environment and meanwhile required by most of the countries of the Federal Republic of Germany. To hold this deadline it must be postulated that the use of high dust SCR technique with ammonia injection proves true.

PRIMARY METHODS

Figure 2 shows, that as well on wet bottom furnaces as on older boilers with dry bottom furnace by reconstruction of the burners during the years 1985 and 1986 to the so-called three stage air type a reduction of the NO_x emissions in the range of 15 to 25 % was obtained. The newer dry bottom boilers are already supplied with low-NO_x burners so that no additional reduction was possible. This relative low NO_x-decrease by primary methods and through that the remaining high concentrations as the starting point for

secondary methods depends on the use of ballast coals in high efficiency furnaces. These chambers don't allow neither further reduction of furnace temperature nor changing of flame envelope. Further the ashes of VKR powerplants are used in the building industry, so the content of carbon in the ash must be smaller than 5 %.

SCR PILOTPLANTS

As the space of time to realize retrofitting of old powerplants with DENOX units is limited to a short period VKR has chosen the SCR technique for testing respectively for insert at their powerplants, because by the experience and practice with Japanese plants a basement is given and the general function-ability is demonstrated.

To proof this SCR technic for boilers fired with high ballast containing coal and to compare these dates with a furnace burning high quality coal, i.e. with Japanese conditions, VKR operates since the end of 1984 up to 8 pilotplants at the same time. Thereby for about one year first always 2 units were running parallel with fluegases of different boilertypes and coal qualities. Beside the high dust variant also the type with fluegas downstream a FGD, i.e. fluegas with low dust- and low sulphur-content is checked. These pilotplants are operated with approximately 1,600 m³/h fluegas and the tested catalysts of different manufacturers have reached meanwhile up to 10,000 operating hours.

Table 1 gives a summary and same facts of the different pilotplants. The tests have shown, that on principle both high NO_x reductions and low slip rates can be realized. On the other side activity losses were found, which partially laid clear above the expectations deducted from Japanese units.

At measurements on pilotplants often it causes some difficulties to differ between activity loss of the catalyst and dirtying by flyash. Nevertheless realistic statements can be deducted:

With fluegas of a boiler burning high quality coal in a dry bottom furnace the same amount of activity loss is found with high dust SCR technic as in Japanese plants.

The damage of catalysts activity is somewhat stronger downstream of ballastcoal fired dry bottom boilers and wet bottom furnaces without fly ash recycling. But the values can be still honoured.

At the high ash side of wet bottom boilers with flyash recycling the originally tested catalysts ran out of activity very quick belonging to the arsenic concentration in the gasphase of the fluegas between furnace and electrostatic precipitator. By enrichment of arsenic on the surface of the catalyst the activity decreases in less than 1,000 operating hours to about 50 %. Catalysts with higher capacity in the startup phase have thereby more reserves against activity loss as such with a lower one.

The catalysts manufacturer are developing new material mixtures with higher resistance against the conditions behind wet bottom furnaces with flyash recycling. In VKR pilotplants meanwhile some specimen with better resistance to arsenic are tested but still the available operation period isn't sufficient.

The low dust version, i.e. the SCR unit downstream a wet FGD plant, is - however more expensive - an alternative method for boilers with melting chamber and flyash recycling. Catalysts in the fluegas stream behind a wet FGD system (and reheated to the catalysts reaction temperature) will not run the risk to be influenced by harmful components. They are very active and lose their activity only at operating temperatures lower than 300 °C by ammonia-bisulfate scaling. This reduction in activity can be reactivated by torching at higher temperatures.

SCR DEMONSTRATION PLANTS

Already running the pilotplants it was found that scaling by flyash is a main problem. As it is impossible to simulate the operation conditions of a large boilerplant by pilotplants relative to NO_x-, ammonia- and dust-distribution across the duct-cross-section, two large testunits were erected and taken into operation:

1. District heating plant (FWK) Buer

The new powerplant was retrofitted at the end of the erection time with a DENOX plant for the total fluegas volume of 500,000 m³/h at the downcoming fluegas duct (between boiler-outlet at the roof and air preheater) without any fluegas bypass. The unit is planned for baseload, producing mainly industrial steam and hot water for district heating. The fuel- and fluegas-data of the boiler are shown on table 2. The dates of the DENOX plant are given on table 3. The flowsheet of the system presents figure 3.

The FWK (including the units for environmental protection like DENOX and FGD) was started at the end of 1985 and the catalysts meanwhile are in contact with the fluegas for more than 8,000 hours.

At the moment when the pilotplant-tests have shown that coarse ash particles are withdrawn from the boiler to the surface of the catalysts with a diameter larger than the inner diameter of the honeycombs, additionally a multicyclone was ordered and installed just at the startup-phase of the plant. This coarse ash separator is placed in the duct-corner of the horizontal fluegas outlet from the boiler and the vertical downcomer ahead the SCR reactor.

These 900 cyclones and the primary mounted fluegas-rectifiers influenced the fluegas- and ammonia-distribution very unfavourable. With gasflowtests these fluegas-rectifiers downstream the multicyclone were optimized so that in the flow region against the catalysts the fluegas was distributed uniformly so that the values varied only $\pm 10\%$ around the average. Also the NO_x profile was very constant.

In comparison with that it failed to find a good ammonia distribution across the catalysts layers. The NO_x values varied $\pm 70\%$ around the average behind the second layer of catalysts. Therefore the ammonia injection was displaced to a higher level and the pressure of the supporting air was raised. With a new ammonia-dosing 7 m above the first layer the NO_x reduction behind the second layer was improved to $\pm 25\%$ around the average. Although this distribution is still very inhomogeneous the manufacturer is certain of obtaining the expected operation period.

The ammonia-control looks very simple: Fluegas through-put, its temperature and the rawgas NO_x concentration are measured and with the given cleangas NO_x value of 98 ppm (gasphase) the necessary amount of ammonia is calculated. An additional measuring of ammonia slip is not installed as with continuously measuring instruments for such small values up to now no satisfaction was attainable. Instead of measuring the ammonia slip the ammonia concentration on the flyash is controlled. Thereby for the conditions of FWK Buer an ammonia-amount of 100 mg/kg in the flyash represents an ammonia slip of 5 ppm. With such a representative sample per day it is possible to determine the average of slip very exact. So the increasing ammonia values in August and at the end of 1986 signalized more rapidly than the pressure-loss measurement that the catalysts where clogged by flyash, see figure 4. The tendency toward pollution in a heavy dustloaded fluegas is important. To keep the plugging inside limits the catalysts are cleaned by steam-sootblowers two times per day. Nevertheless it is impossible to keep all partial areas free from plugging:

On top of sampling- and injection-tubes the dust grows up and these deposits fall down on the catalysts. A part of these dust-cornices remain on the steel grate on top of the catalysts and can be blown off by sootblowers. The other part falls into the honeycomb holes and closes the tubes. Most of this dust is not within reach of sootblowers; the so-plugged honeycomb-zones are easy to identify from their bottom side. Although the rectifier-steel-plates of the first layer have a pitch of 50 mm, the cross-sections grow together by ash as the fluegas-stream has still a horizontal velocity-component. Further the dust settles at all mounting parts last not least even on high pitched bearers. Therefore a great amount of attention is necessary to find the favourable shaping of the things built in the region of the catalysts.

Although the main part of dust deposits and plugging can be collected by exhaust ventilation during boiler standby about 10 % of the honeycombs are closed permanent.

At the last inspection of the catalysts in the top layer 3 areas were found in which dust jets have damaged in a small limited section the catalyst blocks, see figure 5. About 1 to 2 % of the inserted catalysts are affected at this time, so there is no occasion to be in trouble. The reason of these dust jets is not localized till now.

Although these local limited erosions and the partial plugged sections the catalyst itself operated satisfactory for more than 8,000 hours. The NO_x reduction of 75 % was observed. The ammonia slip was in the range of 1 to 2 ppm, partially lower than 1 ppm. The loss of activity of the honeycomb-catalysts is at this time approximately at 15 %. The operation period with the first loading is scheduled for 16,000 hours. After renewing a third of the catalysts an additional operation-time of 8,000 hours shall be obtained.

2. Boilerplant Knepper C

This boiler (see table 2) with a melting chamber without flyash-recycling from ESP was retrofitted with a high dust SCR unit handling 50 % of the fluegas-volume of the 370 MW powerplant. The system was erected in 1 1/2 years and is in operation since mid 1986, sponsored by the Federal Bureau of Environment (UBA) of the Federal Republic of Germany. For the scheduled test-period of 3 years 40 % of the operation-costs are also paid by UBA.

The start-up phase of the demonstration unit was handled without problems. To have the chance of testing different types of catalysts, also to render possible for German manufacturers to test their products, the DENOX plant was divided into two parallel lines. One half of the reactor is loaded with honeycomb-, the other one with plate-catalysts (see table 3).

The fluegas, withdrawn from the lower part of the second boiler pass, is feeded through a horizontal, then vertical mounting duct to the coarse flyash separator. This coarse particle separator isn't like FWK Buer a multi-cyclone but consists of U-profile steelbearers, fixed with the open profile against the fluegas flow.

After that, the fluegas duct is divided into two separate ducts. The ammonia injections are mounted in the horizontal part of this channel. The ammonia dosings of both lines are operated and controlled separate. The simple control for ammonia handling is identical to the unit at FWK Buer.

With a horizontal and vertical 90° turn around the fluegases are passed by the blowerdome into the catalyst-layers, shown in figure 6. At the bottom of the divided reactor the fluegases return to the air preheater inlet of the boiler. The fluegas-duct has a bypass-butterfly-valve not for standard operation but only in cases of malfunctions.

The fluegas distribution along the cross-section was measured downstream of the first layer. It has shown for both catalyst-systems divergences from the average value up to + 35 %. Thereby it was found that at the plate-side, installed inside of the 90° fluegas-corner, a large separation turbulence with backflow exists. The first inspection of the unit has therefore shown large deposits of dust across several catalyst-layers on the plate reactor as shown in figure 7.

As the manufacturer hasn't mounted sootblowers, these sedimentations cannot be blown off. In contrast the honeycomb-catalysts are working under better equalized flux conditions and additional blown with steam-sootblowers ahead of each boiler turn-down as recommended by the manufacturer. These catalysts therefore looked very clean as it was found at the SCR unit of FWK Buer after an operation-period of 3 to 4 months.

Since the turn of the year 1986/87, i.e. after approx. 4,000 hours of operation of the SCR unit, additional alterations came forward:

As done at FWK Buer also at the SCR demonstration unit at Knepper C the slip of ammonia is controlled each day by measuring the ammonia concentration on the flyash, sampled from the ESP. Thereby at the beginning of January 1987 an ammonia increase in the flyash was obtained indicating an ammonia slip higher than 1 ppm. After this short period of 4,000 hours a slip still smaller 1 ppm was expected.

Further the pressure-loss of both catalyst-lines increased from 6 mbar at the plates-side and 8 mbar at the honeycombs-side at the beginning along with the operation-time, see figure 8. Meanwhile the pressure-loss at the plate is higher than at the honeycomb. Even with quite opened butterfly-control-valve at this time only a smaller portion of fluegas passes the plate-catalysts.

As the main reason for these effects the plugging of the catalysts was recognized. Therefore at the scheduled modification of the fluegas-guide-plates to equalize the flux conditions also the flyash deposits must be collected by exhaust ventilation to reproduce the layout conditions. If then it will be necessary to install sootblowers also at the plate-catalysts-side for the periodical cleaning during operation of the unit under the high ash conditions of Knepper C, is not clear now by reason of the disadvantageous conditions of fluegas flux at the inlet side.

Meanwhile also the pressure-loss of the air preheater of the DENOX fluegas-side increased about 30 % in relation to the conditions of the fluegas-side without SCR unit. As after an operation period of 6 months with an ammonia slip for most of the time of less than 1 ppm it will be unlikely that larger ammoniabisulfate-scaling has taken place. So it is guessed that an increase of scaling by falling below the sulphuric acid dewpoint inside the air preheater has happened. The necessary high activity of the catalysts effects therefore a higher conversion rate from sulphur dioxide to sulphur trioxide. As well by the cold air temperatures during wintertime as by the temperature decrease of the fluegas during partial load boiler-operation the temperature on the metal sheets of the air preheater falls down so deep, that condensation at the cold end of the air preheater arise. It is meanwhile impossible, also with higher blower-pressure, to clean the metal sheets. Therefore the air preheater must be washed during the boiler stand-by at spring 1987.

To save the boilerplant-operation from further increasing of pressure loss at the air preheater the NOx cleangas value was raised to about 200 ppm. The efficiency therefore is reduced now to about 80 %, but the ammonia slip has returned to 1 ppm approx.

COSTS

The amount of investment for the honeycombs at FWK Buer ran up to 20 million DM. The ammonia supply occurs by a pipeline.

For the installation of the honeycomb- and plate-catalysts unit for handling 50 % of the fluegases of the boilerplant Knepper C an amount of 25 million DM was invested including the ammonia tanks.

To deduct from these demonstration units already today the total costs of such SCR plants would be untimely. The total costs of SCR plants are mainly influenced by the lifetime of the catalysts and just therefore the testruns are full in progress.

If it would be possible to reach with catalysts at the high dust side operation periods of 2 to 3 years, corresponding to 16,000 hours, without changing catalyst-material, so the total cost of such a unit would be in the range of 0.01 DM/kWh for a boiler size of 350 to 700 MW operating approx. 4,000 hrs/yr full load. This would come up to 50 % of the specific costs, which VKR has to spend for desulfurization of their boilers.

The total costs of investment for retrofitting all VKR boilerplants with FGD- and DENOX-plants within the bounds of the ordinance on large firing installations are estimated in the range of 1.3 billion DM.

SUMMARY

For retrofitting all existing boilerplants with environmental protection installations the authorities have fixed very tight terms. From the feasible techniques to reduce NO_x by secondary methods, from which the main part is still in the development phase, VKR has chosen the system of Selective Catalytic Reduction. Therefore partially it was possible to refer to experiences which are accumulated since 1980 at Japan.

Therefore one of both oilfired 714-MW-blocks at Scholven, which are operated common by Rheinisch-Westfälisches Elektrizitätswerk (RWE) and VKR, is already retrofitted with SCR unit since October 1986. The second block follows with a SCR installation till autumn 1987. RWE owns 50 % of both boilers.

To test this SCR technic for coalfired boilers, specially for furnaces burning high ballast containing coal, since 1984 several pilotplants are running. The tests have shown, that the necessary efficiency up to 90 % is possible but the high flyash concentration in the fluegas can plug the catalysts.

For slag tap fired boilers with flyash recycling from ESP up to now no suitable catalyst was found. By reason of the arsenic-enriching in the fluegas-flyash-cycle the catalysts are poisoned and loss their activity in a short time. The manufacturers are trying to develop arsenic-resistant catalysts. As a possible alternative for high dust technology tests are running on the low dust side, i.e. with reheated fluegases downstream of FGD-plants.

The operation of two demonstration plants at FWK Buer and boilerplant Knepper C shows, that the efficiencies of 75 respectively 90 % called for in these cases are attainable with large units. Certainly the problem of dust deposits even by sootblowing must be solved and the catalysts-erosion must be observed. A shut-down of the boilers as a result of malfunction at the SCR units neither at FWK Buer nor at Knepper C was necessary.

As far as the expectations by the operation of the SCR pilot- and demonstration plants will be confirmed, VKR then will have finished the retrofitting of all large boilerplants at the end of 1990.

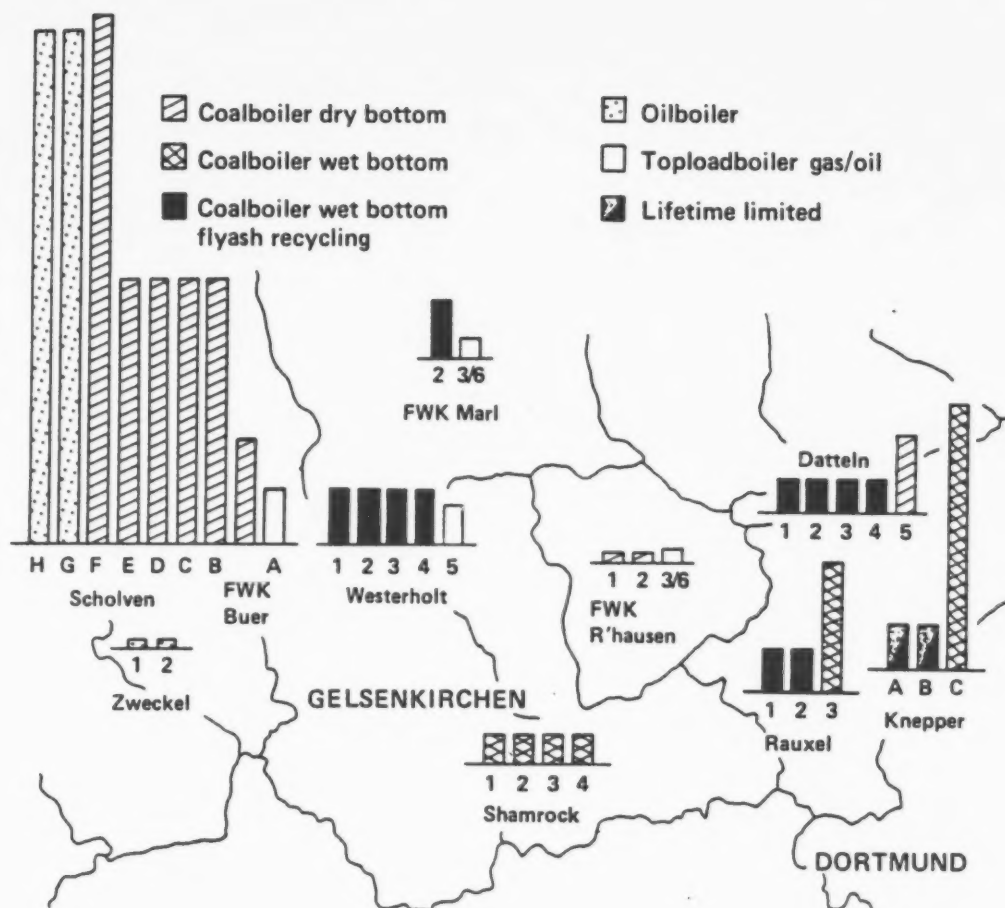


FIGURE 1. SURVEY ON BOILERTYPES AND KIND OF FUEL AT VKR POWERPLANTS

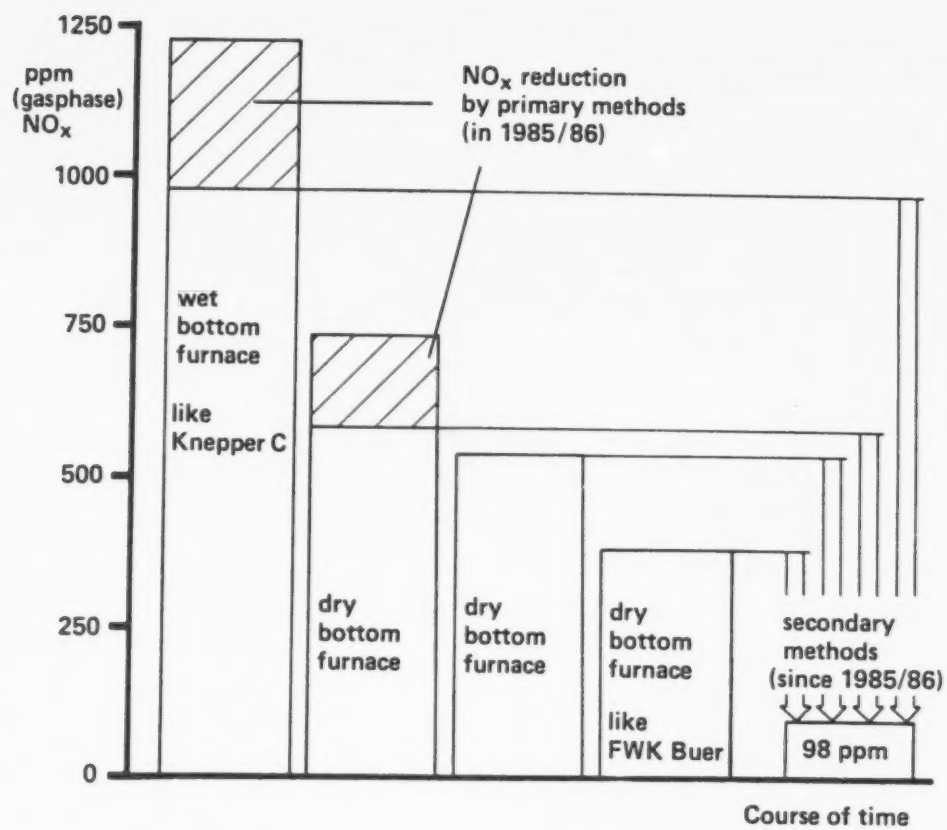


FIGURE 2. STEPS FOR NO_x REDUCTION AT VKR POWERPLANTS

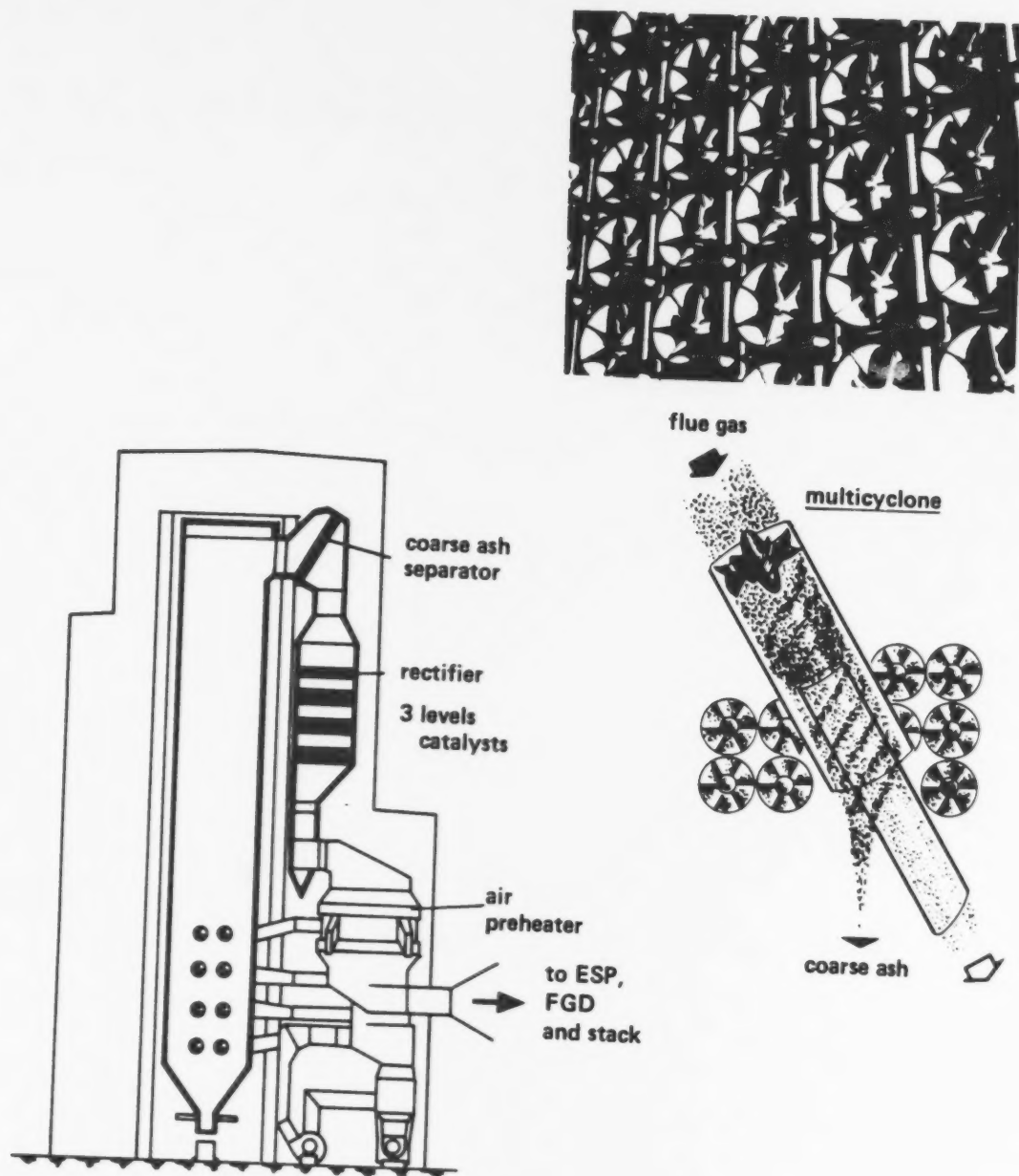


FIGURE 3. DENOX PLANT FWK BUER

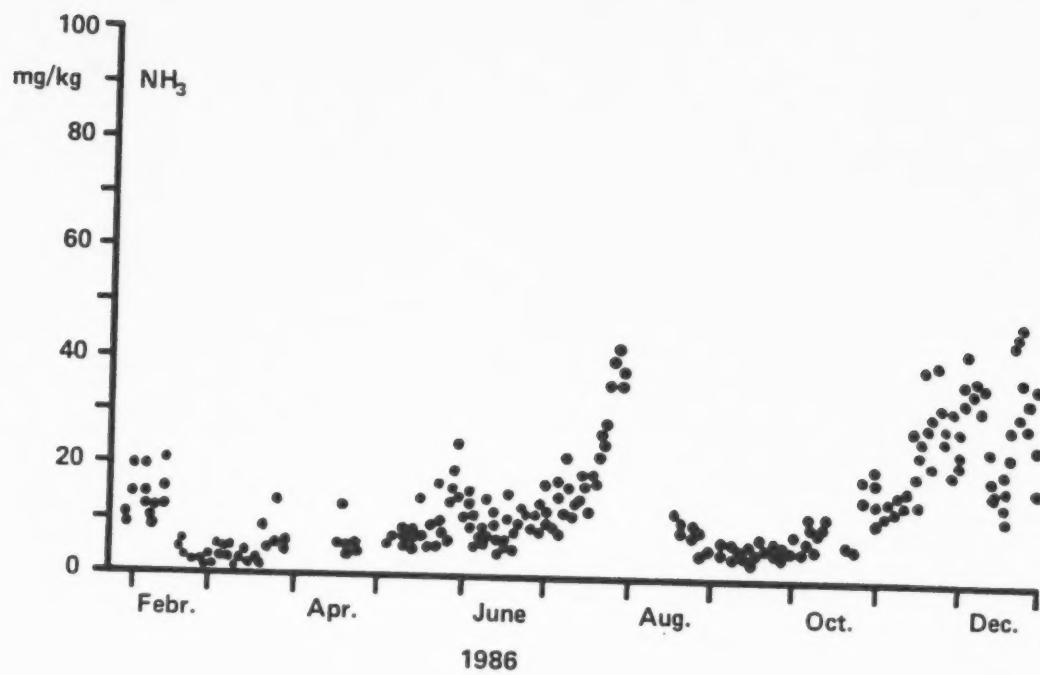
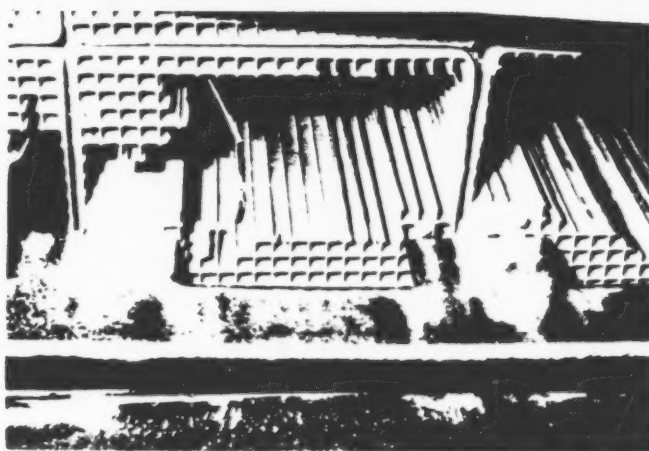


FIGURE 4. FWK BUER - NH_3 IN FLYASH OF ESP

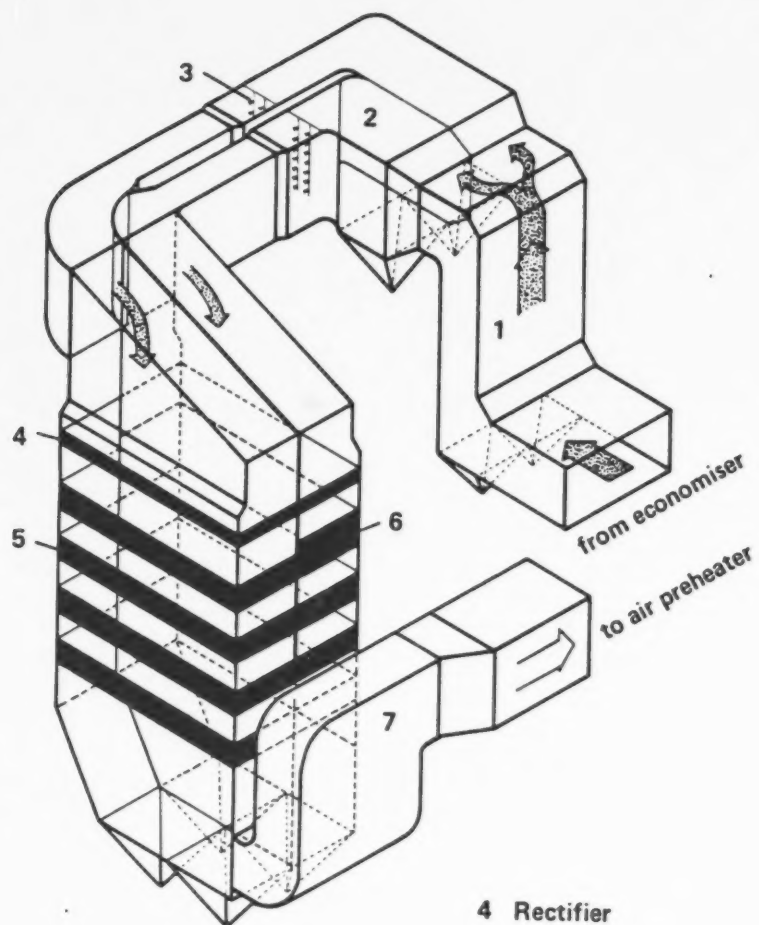


View from above



View from below

FIGURE 5. DENOX PLANT FWK BUE
DAMAGES BY DUST-EROSION AT THE CATALYSTS



1 Raw gas inlet

2 Coarse ash separator

3 Ammonia injection

4 Rectifier

5 Honeycomb cat.

6 Plate catalyst

7 Clean gas outlet

FIGURE 6. DENOX PLANT KNEPPER C

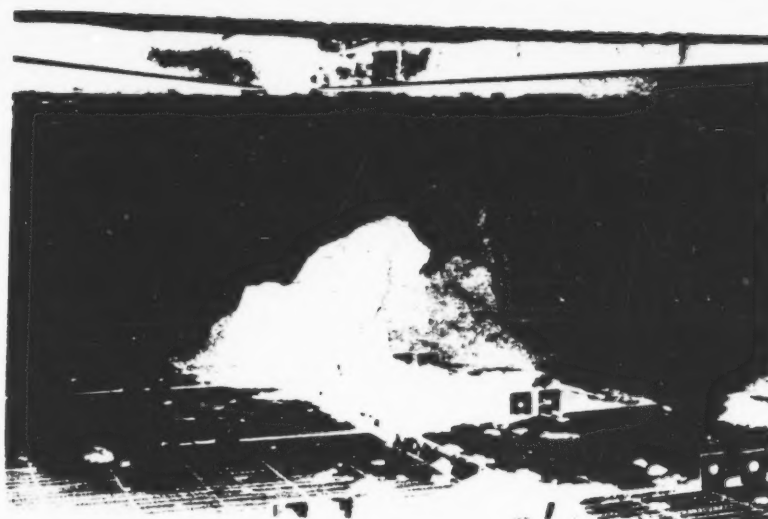
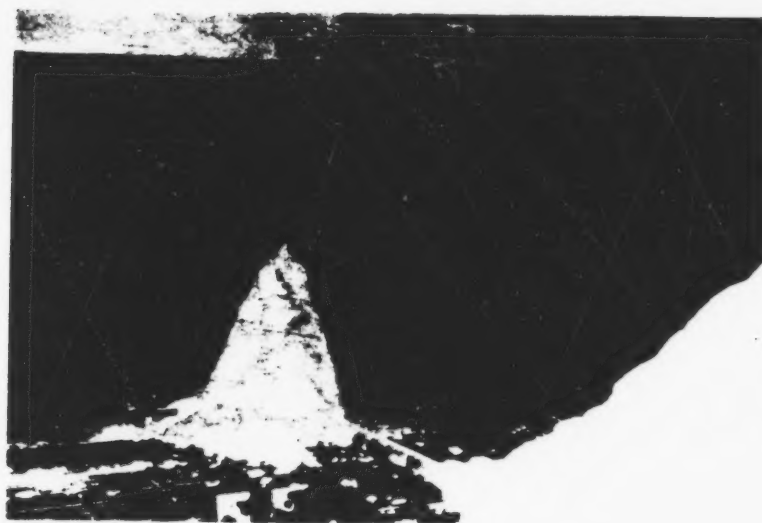


FIGURE 7. DENOX PLANT KNEPPER C
FLYASH DEPOSITS ON THE 2. LAYER

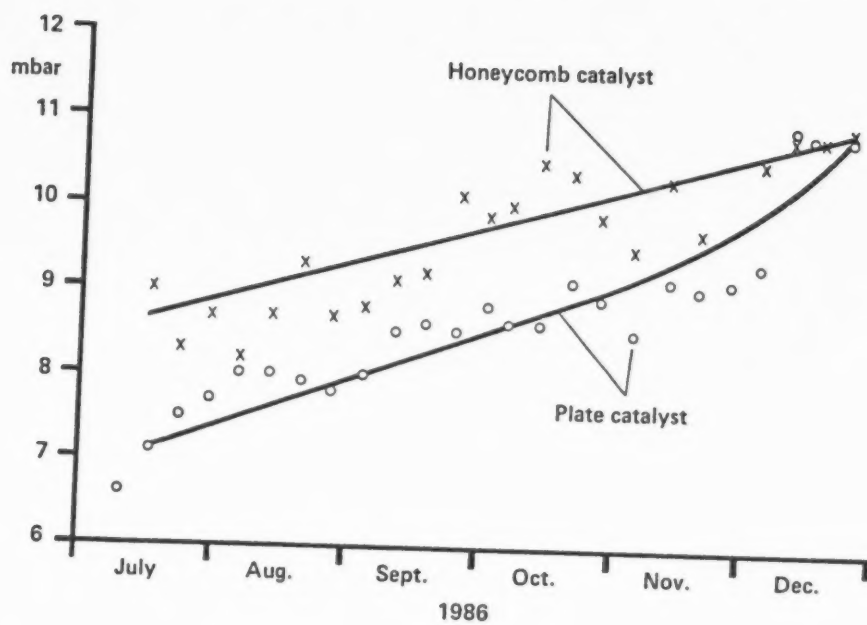


FIGURE 8. DENOX PLANT KNEPPER C - INCREASE OF PRESSURE-LOSS

TABLE 1. DENOX-PILOTPLANTS AT VKR

Boiler	Scholven F		Scholven D	Knepper C	Datteln 3
Furnace Type	Dry bottom			Wet bottom	
Coal Type	High quality		Ballast	Ballast	
Ash Recycling	-		-	Without	With
Catalysts					
- Site	Low dust*	High dust	High dust	High dust	High dust
- Levels	3	3	3	3	2 only
- Efficiency ⁺	78 %	78 %	83 %	90 %	-
- Duration of Test	≤5,000 h	≤10,000 h	≤10,000 h	≤10,000 h	≤1,300 h
- Number of Types tested	4	3	5	2	3

*Downstream FGD (tailgas system)

⁺Based on 98 ppm NO_x clean gas side

TABLE 2. BOILER-, FUEL- AND FLUEGAS-DATES
OF FWK BUER AND KNEPPER C

COMPONENTS		FWK BUER	KNEPPER C
1. <u>Boiler</u>			
- Thermal Rating	MW, th.	383	880
- Electrical Power	MW, gross	146	370
- Start up	m/yr	12/85	1971
- Steam Pressure/Temp.	bar/°C	281/540	227/535
- Kind of Furnace	-	Front firing, dry bottom	Stage-U-firing, melting chamber
- Amount of Burners	-	4 x 2	8 x 2
- Burner Type	-	Stage-mixing burner	
2. <u>Fuel</u>	-	Hardcoal (Ruhrdistrict)	
- Heating Value	kJ/kg	15,700	21,980
- Ash max/ a/v	%	38/30	25/23
- Ballast max/ a/v	%	49/41	36/33
- Sulphur max/ a/v	%	1.85/1.3	1.4/1.0
3. <u>Fluegas</u>			
- Volume	m ³ /h	498,000*	1,075,000 ⁺
- Cleaning (Based on Fluegas Volume)			
-- ESP	%	100	100
-- SCR	%	100	50
-- FGD	%	100	(100) ^x

*Based on 1013 mbar, 0 °C, 6 % O₂, dry conditions

⁺Based on 1013 mbar, 0 °C, 5 % O₂, dry conditions

^xunder construction; start up end 1987

TABLE 3. SCR-DEMONSTRATION PLANTS
AT FWK BUER AND KNEPPER C

COMPONENTS		FWK BUER	KNEPPER C	
<u>1. Fluegas Inlet</u>				
Coarse Ash Separator		900 Cyclones	3 Files of U-Profiles	
Temperature	°C	340	380	
Flyash	g/m ³	40	15	
SO ₂	ppm*	1,500	1,000	
SO ₃	ppm*	3	1.5	
NO _x	ppm*	390	980	
Fluegas Volume	m ³ /h	500,000 ⁺	270,000 ^x	270,000 ^x
NH ₃ -Dosing (max.)	kg/h	120	190	190
Mol Ratio NH ₃ /NO _x		0.8	0.9	0.9
<u>2. Reactor</u>				
Sootblower		Steam	Steam	None
Catalyst-Shape		Honeycomb	Honeycomb	Plate
- Space		7 Pitch	7 Pitch	6 mm
- SV	h ⁻¹	2,930	1,900	1,360
- Levels		3	4	4
- Pressure Loss	mbar	10	8	6
<u>3. Fluegas Outlet</u>				
SO ₃	ppm*	11	6 - 11	
NO _x	ppm*	98	98	
NH ₃ Slip	ppm*	1 - 2	1 - 2	

*ppm (Gasphase)

⁺at 1013 mbar, 0 °C, 6 % O₂, dry conditions

^xat 1013 mbar, 0 °C, 5 % O₂, dry conditions

APPLICABILITY OF EUROPEAN SCR EXPERIENCE TO
U.S. UTILITY OPERATION

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Integrated Environmental Control

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ABSTRACT

Approximately 2200 MW of SCR capacity are operating or in start-up in Europe as of February 1987. Five full-scale systems are currently operational in the Federal Republic of Germany and two in Austria. Each unit has logged between 2000 and 6000 hours of operation.

Experience from these SCR installations will assist defining the cost and technical feasibility of SCR for potential U.S. application. This paper discusses the relevant experience anticipated from these and other European installations. Experience that will directly apply to U.S. conditions is summarized, as are topics which are not relevant to U.S. application due to plant design and fuel limitations.

The European SCR installations are first briefly surveyed, and the significant design and operating features reviewed. Relevant experience is categorized into four topics: (1) SCR catalyst design, (2) catalyst lifetime, (3) process control, and (4) plant integration. Finally, issues critical to the analysis of SCR technical feasibility and cost for high sulfur coal-fired plants are summarized.

INTRODUCTION

Recent NO_x limits imposed by several European countries, most notably West Germany and Austria, force the use of selective catalytic reduction (SCR). By 1992 approximately 60,000 MW of SCR capacity are expected to be in service. Currently, five utilities are operating seven full-scale SCR installations (five in the Federal Republic of Germany and two in Austria) totaling over 2200 MW of capacity. By early 1987 each unit had logged between 2000 and 6000 hours of operation.

Experience from Europe will soon be available to supplement that from Japan in evaluating the cost and feasibility of SCR for U.S. application. Data will have been obtained on many of the most critical issues such as catalyst quantity required (e.g. space velocity), catalyst lifetime, and the influence of SCR on overall plant operations. As fuels used in Europe are similar in some respects to U.S. low sulfur fuels, selected aspects of European experience may be directly applicable. However, different trace fuel constituents in the U.S. may prevent a direct transfer of European experience to low sulfur coal-fired plants without

prior pilot-scale tests. More importantly, the interactions between flue gas SO_2 , residual NH_3 and SO_3 , catalyst performance, air heaters, and other environmental control equipment raise questions about the applicability of European experience to high sulfur coal-fired power plants considered candidates for potential acid deposition legislation.

This paper summarizes preliminary experience reported from the seven operating European SCR installations. These plants and key features of their SCR systems are described in Table 1. Detailed reports from two of the power stations are described elsewhere in this session. The role of European experience in providing meaningful input to potential U.S. SCR application is discussed. A summary is presented of the critical issues that need to be addressed to allow rational, fact-based public discussions regarding the cost and applicability of SCR in the U.S.

Relevant topics are discussed under four categories: (1) SCR process design, (2) catalyst lifetime, (3) process control, and (4) plant integration. Costs for various NO_x control strategies that could involve SCR are discussed at the conclusion of this paper.

SCR PROCESSES

Descriptions

SCR can significantly affect plant operation because the reactor is located immediately following the boiler economizer. As a result, the process residual emissions, which are NH_3 and SO_3 , are introduced into the flue gas prior to other environmental controls and flue gas handling equipment. Also, because the SCR reactor is located ahead of the air heater, changes in boiler conditions (e.g., load, excess air level) will alter flue gas temperature and can affect SCR performance.

Figure 1 illustrates several configurations for applying SCR to coal-fired power plants. Each configuration either has been applied at full-scale in Europe or Japan, or is the subject of major engineering and/or pilot-plant studies. Configurations 1a and 1b are the two most common, and differ only in whether the SCR reactor precedes or follows the particulate control device. Configuration 1b, commonly referred to as the "low dust" configuration, has received preference over Configuration 1a (referred to as "high dust") for locations in Japan where contamination of fly ash by residual ammonia reduces the fly ash resale value. As a potential retrofit technology, however, low dust systems are applicable only to the few boilers with "hot" electrostatic precipitators. Both 1a and 1b expose waste water and solids from SO_2 removal to ammonia contamination.

Configurations 1c and 1d illustrate the application of spray drying with SCR. In Configuration 1d fly ash is removed prior to SO_2 byproduct collection, while in Configuration 1c it is removed with the SO_2 byproduct. Spray drying is a net water consuming process and thus ammonium-containing waste water will not exist. However, ammonia will contaminate both fly ash and SO_2 removal byproducts, which can be disposed, treated, or sold either separately (1d) or combined (1c).

Configuration 1e illustrates one concept for applying SCR downstream of all control equipment, thus preventing ammonia from contaminating fly ash, waste water, or SO_2 removal byproduct. This approach, currently under construction at the Heilbronn station of EVS in West Germany and commonly referred to as "cold-side" SCR, requires reheating flue gas to SCR operating temperatures (600-700°F). The cost and feasibility of this approach will depend on the plant heat rate penalty,

which could be minimized by development of efficient regenerative heat exchangers and low temperature catalysts.

Currently all seven SCR installations in Europe are high dust systems. Three of the SCR installations are followed only by an ESP, with presently no FGD equipment. However, two of these plants are being retrofitted with wet FGD (Configuration 1a) and one with spray dry/fabric filter (Configuration 1c). Two additional SCR installations are followed by both ESP and wet FGD (Configuration 1a), and two by and ESP and spray dry/ESP (Configuration 1d).

COSTS

Previous engineering studies conducted for EPRI evaluated the cost of SCR for low-and high-sulfur coals.⁽¹⁾ This analysis used operating experience with a 2.5 MW(e) SCR pilot plant at the EPRI Arapahoe Test Facility as a basis to evaluate SCR capital and operating costs for new 500 MW coal-fired power plants.⁽²⁾ Depending on initial NO_x concentration, percent NO_x removal required, and fuel composition, SCR capital costs were projected to range between 60-107 \$/kW (end-of-year 1985 \$). The corresponding levelized costs, reflecting both capital and operating expenditures, were 6.2-16.4 mills/kWh for a 30-year plant life and a one-year catalyst lifetime. Sensitivity studies showed that increasing catalyst lifetime from 1 to 2 years reduced levelized costs by approximately 35%. For the case of low sulfur coal, this corresponded to a decrease from 8.4-16.4 mills/kWh to 5.7-10.9 mills/kWh. These results demonstrated that catalyst lifetime dominates the total levelized cost of SCR and that accurate predictions of lifetime are critical for credible cost estimates.

SCR costs obtained from two European installations discussed in this paper were generally consistent with EPRI estimates. Costs for retrofit to plants in the 300-500 MW generating capacity range were 75-100 \$/kW, and levelized costs accounting for a 2-3 year catalyst life were approximately 5 to 10 mills/kWh. These costs were converted to U.S. dollars with September 1986 currency exchange rates.

CATALYST DESIGN

Background

The design of an SCR process is a trade-off between higher plant costs incurred from residual NH_3 and SO_3 , versus higher catalyst cost to minimize their concentration. Preferably, full-scale or pilot plant experience at meaningful conditions is available to determine the maximum NH_3 and SO_3 concentration that can be tolerated. The catalyst is then designed to produce residual NH_3 and SO_3 not exceeding these levels. For the low sulfur coals to which SCR has been applied, catalyst design generally consists of selecting (1) space velocity to control residual NH_3 , and (2) composition to minimize SO_2 to SO_3 oxidation.

Catalyst space velocity and thus cost are governed principally by NO_x removal, initial NO_x concentration, and allowable residual NH_3 . Requiring either higher NO_x removal, lower residual NH_3 , or operating at high initial NO_x concentration will necessitate the use of low catalyst space velocity (e.g., large catalyst and consequently high cost). The last incremental quantity of catalyst is added to minimize residual NH_3 below an acceptable level. Lower space velocity, although beneficial to reducing residual NH_3 concentration, can increase SO_2 to SO_3 oxidation. For fuels with high sulfur content or low fly ash alkalinity, high SO_3 production may limit space velocity. Thus, simultaneously achieving low residual NH_3 , low SO_3 , and meeting NO_x removal may not be possible for higher sulfur fuels.

European Experience

Figures 2 and 3 summarize the catalyst space velocity and geometry for the seven full-scale SCR installations currently operating in Europe. Figure 2 shows the relationship between space velocity and design NO_x removal efficiency, and Figure 3 the relationship between space velocity and initial NO_x concentration. Also indicated on the figures is the catalyst type: plate or honeycomb. For all cases the NO_x removal target is 200 mg/m^3 at 6% O_2 (120 ppm at 3% O_2) or less, and residual ammonia is predicted by the catalyst developers to be less than 5 ppm for the guarantee period (12,000 or 16,000 hrs depending on the installation). All plants report meeting NO_x removal requirements with flue gas NH_3 concentration of 2 ppm or less.

Figure 2 shows a consistency between design catalyst space velocity and the design NO_x removal for the seven SCR installations. The only exception is the honeycomb-type catalyst at plant E, which appears undersized in comparison to the other installations. Note that there is a significant difference for plants C and E between the design and planned operating NO_x removal. Catalyst space velocity appears to decrease in direct proportion to required NO_x removal efficiency.

Figure 3 shows how space velocity decreases as NO_x inlet concentration increases. The plant E catalyst again appears undersized given the design initial NO_x concentration. Other factors (e.g., space available for retrofit) may have dictated selection of space velocity for this plant. Figure 3 shows space velocity decreases in direct proportion to NO_x concentration up to 500 ppm, with further NO_x concentration increases having a modest effect.

Figure 4 compares recently published information from SCR in Japan to European data.⁽³⁾ Although it is difficult to generalize with this limited data, Figure 4 suggests space velocity for Japanese SCR installations exhibits a similar relationship with NO_x removal. The wider range in space velocity could be attributable to the greater variation in (a) generating capacity of the plants represented and (b) levels of technology maturity.

Implications For U.S. Application

Experience demonstrating that predicted NO_x removal and residual ammonia concentration can be achieved over the guarantee period would improve confidence in design procedures for low sulfur coals. However, the role of trace species in fly ash indigenous to U.S. low sulfur fuels would not be accounted for. For high sulfur fuels, the key process design issue -- that of simultaneously achieving low residual NH_3 and SO_3 while meeting NO_x removal -- would also not be addressed. This critical information will only be confidently determined with pilot plant tests.

CATALYST LIFETIME

Background

Catalyst lifetime dictates SCR levelized costs. Historically, catalyst lifetime guarantees from different process developers have varied significantly. This is largely due to (a) the limited range of fuel properties for which catalysts have been developed, and (b) the difference in fuel properties to which they have been applied. Until recently, limited long term commercial operation and plant operating experience have contributed to uncertainty in lifetime predictions. For example, catalyst activity for the EPRI Arapahoe SCR pilot plant decreased sooner than

expected, due to high levels of potassium in U.S. ash not accounted for in vendor design.

Two of the principle catalyst deactivation modes are surface masking and poisoning of active sites. Surface masking by sulfate compounds appears to be aggravated by fuel characteristics that promote high SO_2 and SO_3 concentration. These fuel characteristics are high levels of fuel sulfur, high fly ash iron content (which may catalyze the SO_2 to SO_3 oxidation in the boiler), and low ash alkalinity (which can absorb or buffer SO_3).

Other fly ash constituents are known to be important in determining catalyst lifetime. Trace metals in fly ash (e.g. potassium, as noted earlier) have been identified as responsible for premature catalyst deactivation. In addition, high ash silica content produces an abrasive fly ash. Catalyst erosion can be reduced by minimizing gas velocity in the catalyst; however, this could significantly increase catalyst quantity and cost.

European Experience

As the European SCR installations are in early phases of operation, no experience is yet available confirming lifetimes. When available, European experience will span a wide range of fuel properties when compared to typical U.S. low sulfur coals. Figure 5 illustrates the guaranteed catalyst lifetime and the fuel properties of selected European SCR sites. Also shown for comparison are fuel properties of typical U.S. low and high sulfur coals. Fuel properties compared are (1) uncontrolled SO_2 concentration, (2) fly ash alkalinity (excluding Fe_2O_3 content), and (3) fly ash iron content. Figure 5 shows the fuel properties that affect net SO_3 concentration are similar to low sulfur U.S. coal, but differ for high sulfur fuels.

Initial results from pilot plant experience at Rheinisch-Westfälischen Elektrizitätswerk (RWE) with a reportedly abrasive fly ash did not reveal erosion problems. However, as previously discussed, erosion strongly depends on gas velocity in the catalyst. Reportedly the RWE pilot units are 25% oversized, which could increase catalyst tolerance to erosion.

Several European utilities reported SCR installed following a wet bottom furnace with fly ash recycle experienced a significant decrease in catalyst activity. The condensation of arsenic on catalyst surfaces and subsequent poisoning of active sites has been proposed as the cause for activity loss. Both Japanese and German vendors are trying to develop arsenic-resistant catalysts, and one German utility has ordered a high dust SCR for a wet bottom furnace with ash recycle.

Implications For U.S.

Experience in Europe will assist predicting catalyst lifetime for potential low-sulfur U.S. applications. Successfully documenting a two-year life in Europe would suggest that a two-year lifetime may be achievable for U.S. low sulfur fuel. However, fuels similar in total alkalinity and sulfur content may differ in trace element composition, which if not accounted for in catalyst design could reduce lifetime below predicted values.

Regarding high sulfur coals, the effect of significant differences in fuel properties such as sulfur content and alkalinity can only be determined with representative pilot plant testing or full-scale demonstration. For this reason, a large scale demonstration of SCR operation, similar to that recently proposed by Southern Company with EPRI endorsement in response to the DOE Clean Coal

Technology initiative, would be appropriate. Meaningful data obtained from such a facility would allow fact based decisions to be rendered.

PROCESS CONTROL

Background

SCR process controls optimize ammonia injection over the range of plant operating conditions so NO_x removal is achieved without excessive NH_3 emissions. Process controls are most important for NO_x removal above nominally 80%, where small deviations from ammonia injection, NO_x concentration, or catalyst temperature can significantly increase residual NH_3 . Critical process control steps are (1) continuously monitoring ammonia flow rate and the flue gas composition, flow rate, and temperature, and (2) maintaining uniform NH_3/NO_x concentration at the reactor inlet. Control schemes used in the past either maintained constant values of (a) NH_3/NO_x mole ratio at the reactor inlet, or (b) NO_x removal efficiency.

Critical to process control is proper flue gas sample conditioning for gas composition monitors. Experience with the EPRI SCR pilot plant indicated interactions with flue gas constituents and fly ash across sample particulate filters could alter NO_x and NH_3 concentration. Specifically, the ash layer that accumulates on the gas sample filter can provide a media for reduction of NO_x by NH_3 . Sample conditioning system design must minimize the role of interactions with fly ash and other species.

European Experience

Five of the European SCR installations designed for 80% NO_x removal monitor outlet NO_x emissions and adjust ammonia injection to maintain 120 ppm (or less). This control scheme, as well as that of maintaining constant NH_3/NO_x mole ratio and NO_x removal, cannot avoid high NH_3 concentration from process excursions when greater than 80% NO_x removal is required. However, these approaches may be adequate for NO_x removal less than 80%. Any of these control schemes could be used in conjunction with a flue gas ammonia monitor to reduce NH_3 injection in the event of an upset. However, the lack of a commercially available continuous ammonia monitor with high reliability mandatory for process control prevents such schemes. Although several European utilities are working with instrument vendors to improve the commercially available systems and evaluate new designs, none of the current monitors are judged sufficiently accurate and reliable to serve as process control systems.

European experience will assist evaluating: (1) specifications for monitors for injected ammonia feed rate and flue gas flow rate, temperature, and composition; and (2) maintenance procedures and sparing philosophy to insure reliable on-line operation.

Experience to date has already improved ammonia injector design and developed flue gas mixing baffles to insure proper NH_3/NO_x contacting. One utility achieved proper mixing by installing (1) turning vanes prior to the reactor to insure uniform NO_x distribution in the flue gas duct, and (2) orifices on the ammonia injectors to provide a constant NH_3/NO_x mixture across the duct. The turning vane design was established from detailed traverse measurements of NH_3 and NO_x across the flue gas duct. In future applications, injector and duct design could benefit from cold flow modeling studies.

An operating characteristic of SCR potentially affecting process control and residual NH_3 emissions is the capacity of some catalysts to absorb, store, and desorb

ammonia. This characteristic was noted at the EPRI SCR pilot plant and has recently been reported by several European SCR installations. This characteristic manifests itself through changes in NO_x removal efficiency and residual NH_3 concentration up to 12 hours after a process condition change. For example, in one test series with the EPRI SCR pilot plant, NH_3/NO_x ratio was increased to 0.90 from approximately 0.80. Measurements of NO_x removal efficiency and residual ammonia obtained 4 hours after the NH_3/NO_x change were different from measurements obtained 12 hours after the change, with all other variables approximately constant. Specifically, NO_x removal decreased from 88 to 84% and residual ammonia increased from 2 to 3% of injected NH_3 concentration from 4 to 12 hours after the NH_3/NO_x ratio increase. Reductions in NH_3/NO_x had the opposite effect on NO_x removal efficiency and residual ammonia concentration.

This catalyst characteristic could further complicate process control and, if severe enough, could mandate residual ammonia monitoring as a process control input. Experience with varied catalyst designs in Europe will indicate how widespread and significant this characteristic is.

Implication For U.S. Application

Experience in continuous on-line analysis of flue gas may apply directly to U.S. conditions. The major obstacles to direct utilization of experience could be the role of fly ash constituents in interfering with analytical measurements. The sensitivity of the residual ammonia concentration to the uniformity of the inlet flue gas flow and injected ammonia has already alerted designers to the need for cold flow model studies and the use of turning vanes.

Potentially the most significant benefit of European experience would be the development of a continuous on-line ammonia analyzer. In the absence of such a monitor, the utilities are inferring residual ammonia concentrations from ammonia measurements on daily fly ash samples.

PLANT INTEGRATION

Background

The most significant technical uncertainty in considering the applicability of SCR to U.S. conditions may be the effect of residual NH_3 and SO_3 on flue gas handling equipment and other environmental controls. Of concern are air heater operation, particulate and SO_2 controls, and management practices for waste water and solids. Plants that must meet stringent waste disposal requirements in addition to strict flue gas emission limits may require very low residual NH_3 and SO_3 to maintain plant operability and minimize operating costs. The potential for generating new environmental control issues must also be considered, such as disposal of spent catalyst or air heater water wash.

For example, the effect of ammonium sulfate/bisulfate deposition on air heater surfaces and the attendant increase in pressure drop has been well documented. Full-scale tests in Japan, and pilot plant tests in Europe and at the EPRI Arapahoe Test Facility quantified pressure drop increase and evaluated sootblowing and on-line water washing as means to restore pressure drop. In virtually all observations, air heater pressure loss was found to be proportional to the potential for forming ammonium sulfate/bisulfate. Experience at EPDC's Takehara station was responsible for establishing a maximum 5 ppm residual NH_3 at the air heater inlet for this low S (0.8%) coal. Also, concern for residual NH_3 affecting fly ash disposal/resale was one reason initial SCR installations on coal in Japan employed hot-side ESPs to remove fly ash prior to ammonia injection.

Possibly the most significant effect of SCR on plant operation is that of residual NH_3 on FGD, especially the waste water and solids. Residual NH_3 absorbed by scrubber slurry will contribute slightly to slurry alkalinity, and no detrimental effect on SO_2 removal is anticipated. However, the concentrating effect of scrubber water management will elevate slurry ammonium compound content. The final slurry ammonium content, and effect on waste water and solids generated and their management, will depend on specific scrubber design.

European Experience

By 1989 all seven SCR applications currently operating in Europe will also have an FGD, either wet or dry, downstream of the SCR reactor and particulate collector. Thus, data describing the impact of SCR on SO_2 control systems will not be available for half the sites until the early 1990s.

During these first years of SCR operation, with most plants targeting residual NH_3 below 1 ppm, little impact of SCR on air heater pressure drop is anticipated. Useful information on air heater deposits may only emerge if residual NH_3 approaches the guarantee levels of 5 ppm, or deposits accumulate unexpectedly. (See, for example, the preceding paper on VKR's experience.) Since some deposits will occur in the air heaters, all SCR installations will have to develop treatment/disposal techniques for the wash water.

Preliminary observations suggest that approximately 70% of the residual ammonia is adsorbed by or condenses on fly ash. Several stations report an ammonia smell threshold corresponding to a residual concentration of 2.5 -5 ppm in the flue gas. Since a greater fraction of fly ash is resold in Europe than in the U.S., we anticipate considerable effort by European utilities (e.g., potentially reducing usable catalyst life, lower space velocities) to maintain resale value.

Two factors affecting European FGD operation and design may minimize deleterious effects of SCR. First, constraints placed on fly ash quality and/or the reported high rate of ammonia adsorption by fly ash could reduce ammonia carryover to insignificant levels at the FGD inlet. Second, some European FGD designs employ prescrubbers operating at low pH to remove chlorides, primarily to enhance gypsum resale value. These prescrubbers, rare in U.S. FGD design, will likely remove most residual NH_3 and not allow contamination of the primary scrubber slurry. The potential for ammonia contamination will be monitored closely because wet FGD wastes from virtually all hard-coal-fired boilers will be sold commercially as gypsum. Further, recent legislation no longer allows landfilling of spray dryer solid wastes. Consequently, we anticipate considerable effort by European utilities to minimize ammonia contamination of FGD and spray dryer solid waste to maintain reuse and minimize disposal costs.

Regarding catalyst disposal, the Federal Republic of Germany recently prohibited the export of wastes. Therefore, although the original contracts between SCR vendors and operating utilities for all eight installations provide for removal of the spent catalyst by the vendor and disposal outside Germany or Austria, both Japanese vendors and German industrial firms are actively researching catalyst recycle techniques.

Implications For U.S. Application

Several significant differences between European and U.S. fuel composition, flue gas handling equipment, and environmental control equipment complicate transfer of results. Most importantly, for higher sulfur coal, the increased SO_2 level and the corresponding potential for (a) low temperature materials reliability problems, and (b) heat rate penalties are most significant. Most SCR process

vendors and users report that nominally 0.75-1.5% of the inlet SO_2 is oxidized to SO_3 . For a high sulfur coal producing 3000 ppm SO_2 , this could elevate the SO_3 concentration entering the air heater by 30-45 ppm above the already high (relative to European conditions) baseline levels (e.g., 20 ppm). If acid dewpoint induced corrosion cannot be avoided through improved materials of construction, it would be necessary to increase air heater exit temperatures nominally 30-50°F to avoid SO_3 condensation. Each 10°F increase in air heater exit temperature can reduce boiler efficiency by 0.5%, or increase heat rate by up to 35 Btu/kWh. The resulting heat rate penalty, possibly approaching several hundred Btu/kWh, could increase annual fuel costs by 2 percent.

Regarding FGD, differences in design and fuel properties (particularly sulfur content) limit applicability of FGD experience. European FGD systems are expected to operate at higher scrubber cycles of concentration (from lower solids/waste water purge) and under stricter solid waste reuse requirements than their U.S. counterparts. On the other hand, the use of prescrubbers for chloride control in some designs will protect the primary slurry loop and byproduct stream from ammonia contamination. European FGD designs that do not employ prescrubbers and operate with stringent waste management may well model potential U.S. installations.

Solid waste disposal requirements for material that must be landfilled must be considered. Specifically, how fly ash with NH_3 responds to the proposed Toxicity Characteristic Leaching Procedure (TCLP) is an important test European applications will not address.

COST ANALYSIS

Figures 6 and 7 compare SCR costs for several alternative NO_x reduction scenarios. SCR cost estimates are extrapolated from EPRI CS3603, and estimates for reburning costs come from a paper⁽⁴⁾ in this Symposium. Figure 6 shows that for retrofits firing high sulfur coal the cost per ton of NO_2 removed for a strategy providing 90% NO_x control (from nominal pre-NSPS levels of 1.0 lbs/MMBtu) is much greater than for a strategy providing 50% or 75% NO_x control. Only the case of optimistic SCR catalyst life estimates in combination with the highest cost for reburning favor SCR application.

Figure 7 presents a similar comparison for a new unit firing low-sulfur coal, giving SCR the benefit of a 3-year life. For this new application, the boiler would be designed with advanced combustion modifications to achieve NO_x levels that are 50 to 75% below pre-NSPS levels (e.g., 0.25 to 0.5 lb/MMBtu). If such a boiler must comply with a NO_x limit equivalent to a 90% reduction from pre-NSPS levels, additional SCR reduction of 60 to 80% could be considered, depending on combustion modification capabilities. NO_x removal costs of such a scenario range from \$1,100 to 1,650/ton NO_2 removed by SCR compared to \$100 to 200/ton for low- NO_x burners.

These cost estimates, as well as those cited earlier, assume that ammonia will remain widely available at current prices (plus normal inflation). The potential impact on the availability and price of ammonia from a rapid, large increase in demand due to legislation requiring extensive SCR retrofit are not considered in these analyses.

CONCLUSIONS

Future European experience with SCR, typified by the preliminary reports from the seven installations described in this paper, is anticipated to:

- (1) Improve confidence in determining catalyst space velocity and predicting catalyst lifetime for low sulfur coals. European experience may establish a two-year catalyst lifetime in cost estimates for potential applications to low sulfur fuel in the U.S., barring premature catalyst deactivation from trace metals indigenous to U.S. coals (e.g., potassium). Premature catalyst deactivation by arsenic as reported by European utilities is an example of an unanticipated effect that could impact U.S. application.

Pilot plant tests are critically needed to evaluate SCR application to high sulfur U.S. coals. The combination of higher fuel sulfur content, greater potential for SO_3 (from increased SO_2 , iron content, and reduced alkalinity) and unknown effects of trace elements indigenous to U.S. coals necessitates additional experience before technical feasibility and costs can be established.

- (2) Define engineering refinements to improve process controls. Many lessons regarding process control will be directly transferrable - such as obtaining good NH_3/NO_x mixing and uniform distribution at the SCR reactor inlet. Design and maintenance practices of flue gas monitoring/diagnostic equipment may apply directly, barring flue gas sample transformation due to trace metals. The significance of catalyst ammonia adsorption/desorption will be defined for a variety of catalyst materials.

If a continuous ammonia monitor is developed in response to the large demand in Europe, it may be one of the greatest benefits of the European experience to potential U.S. applications. Successful monitor designs and sample gas conditioning equipment must still be calibrated in the presence of fly ash typical of U.S. coals to insure adequate performance.

- (3) Provide limited lessons on the potential impacts of SCR on the air heater, FGD, or liquid and solid waste management due to the low levels of residual ammonia. SCR operation to maintain high solid waste resale, and the predominant use of prescrubbers for chloride control, minimize applicability of this category of European experience to U.S. conditions.

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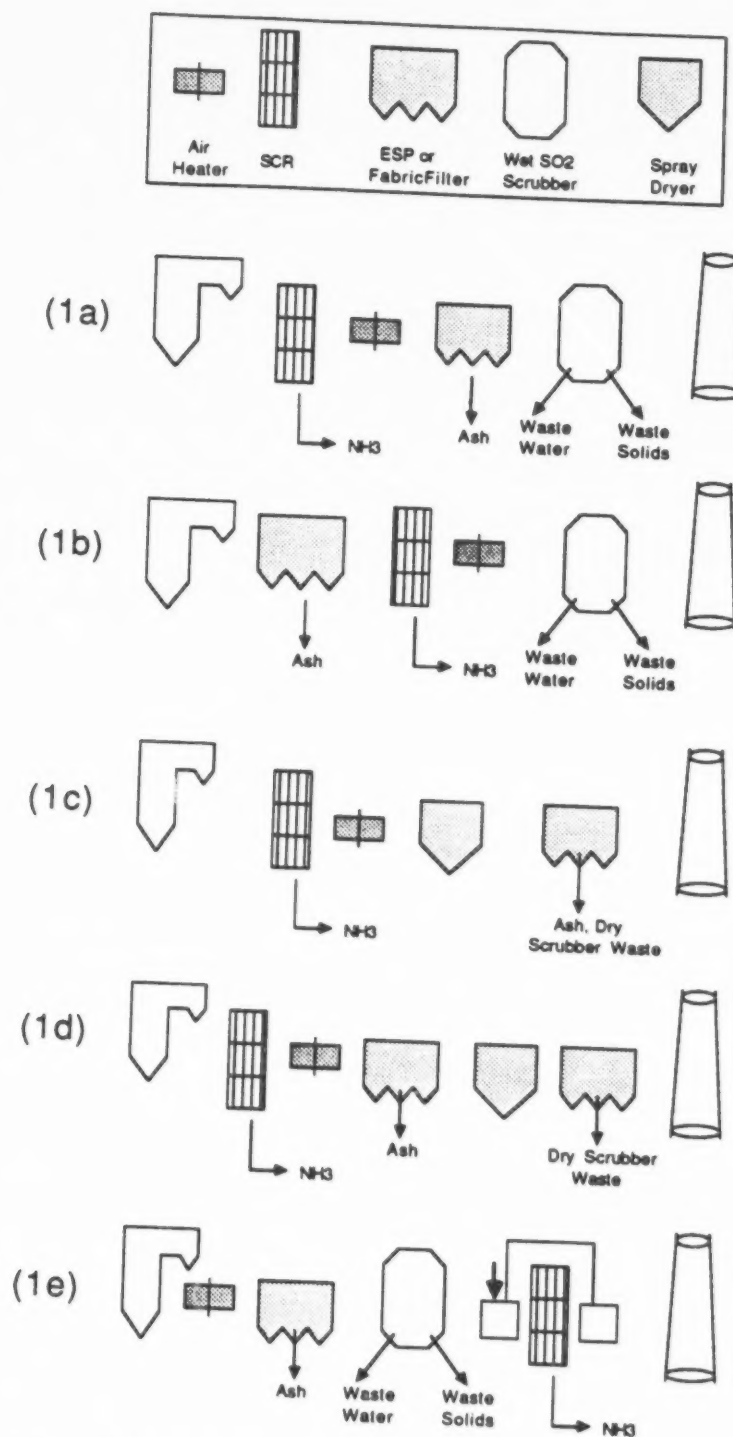


FIGURE 1. POSSIBLE SCR CONFIGURATIONS

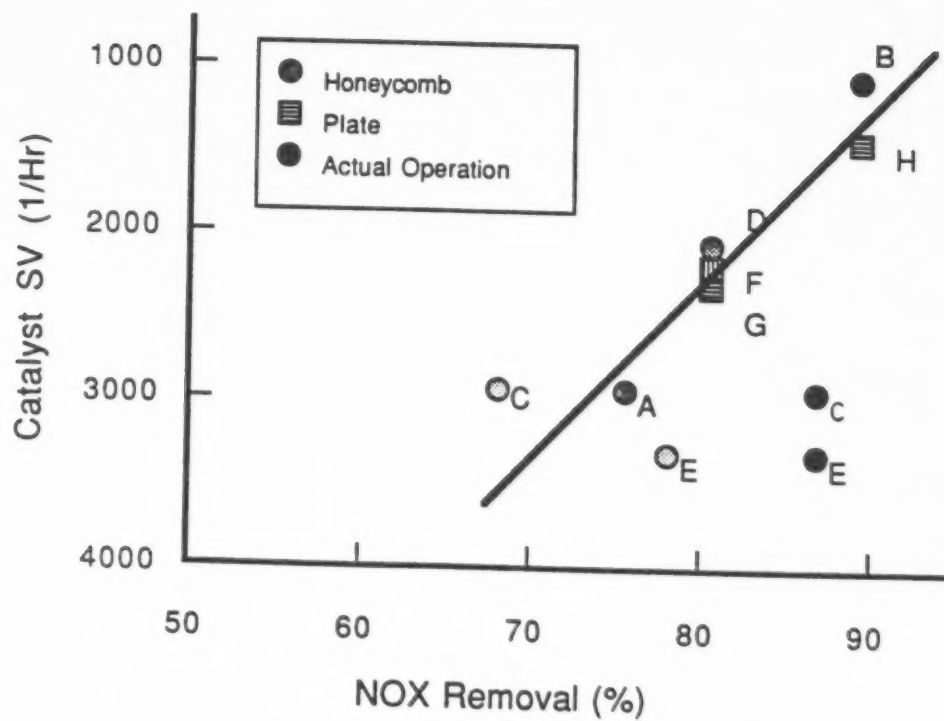


**FIGURE 2. CATALYST SPACE VELOCITY
Vs. NO_x REMOVAL EFFICIENCY**

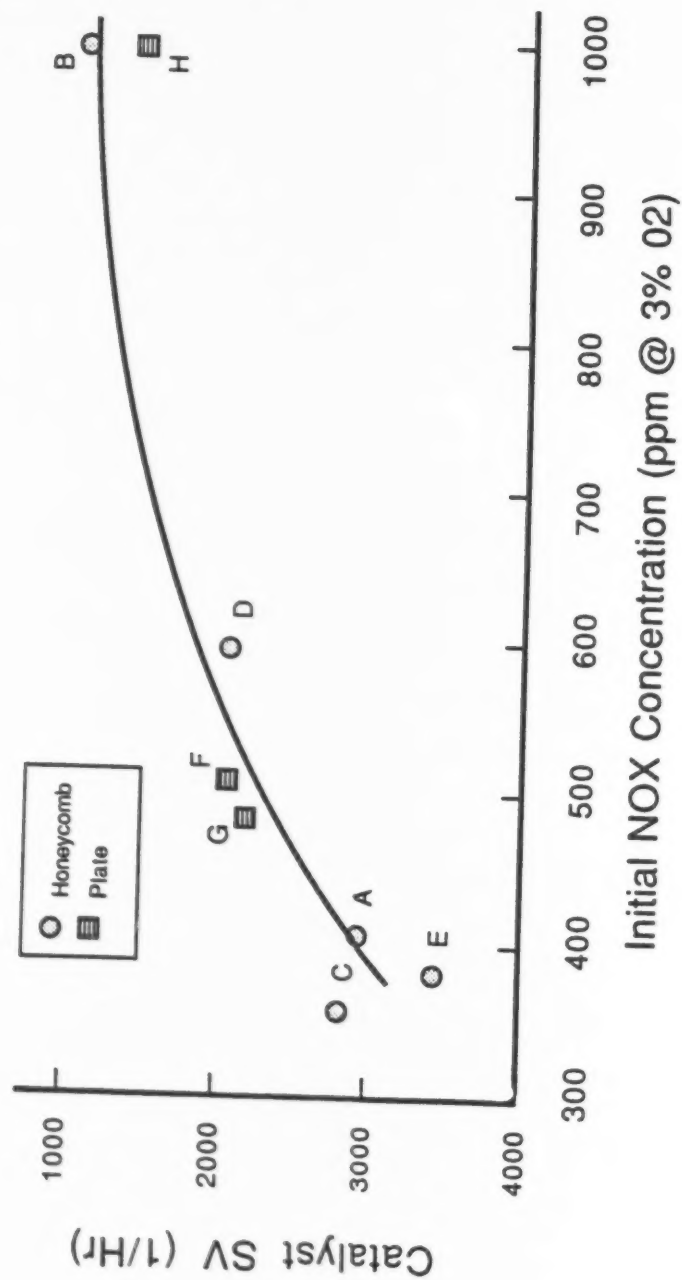


**FIGURE 3. CATALYST SPACE VELOCITY
Vs. INITIAL NOx CONCENTRATION**

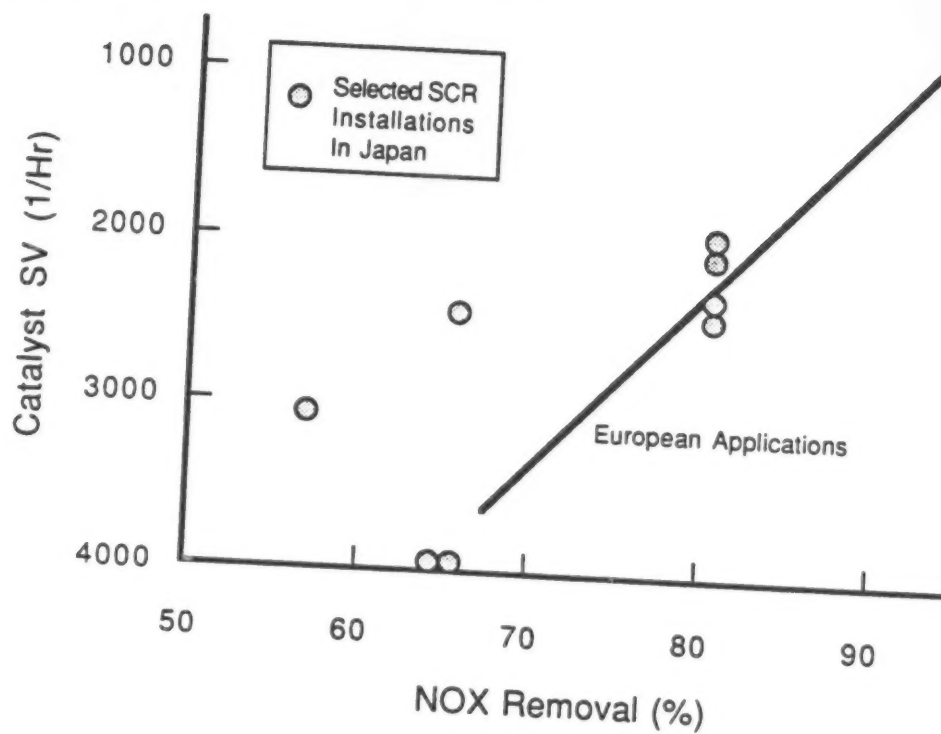


**FIGURE 4. SPACE VELOCITY COMPARISON:
EUROPEAN VS. JAPANESE INSTALLATIONS**

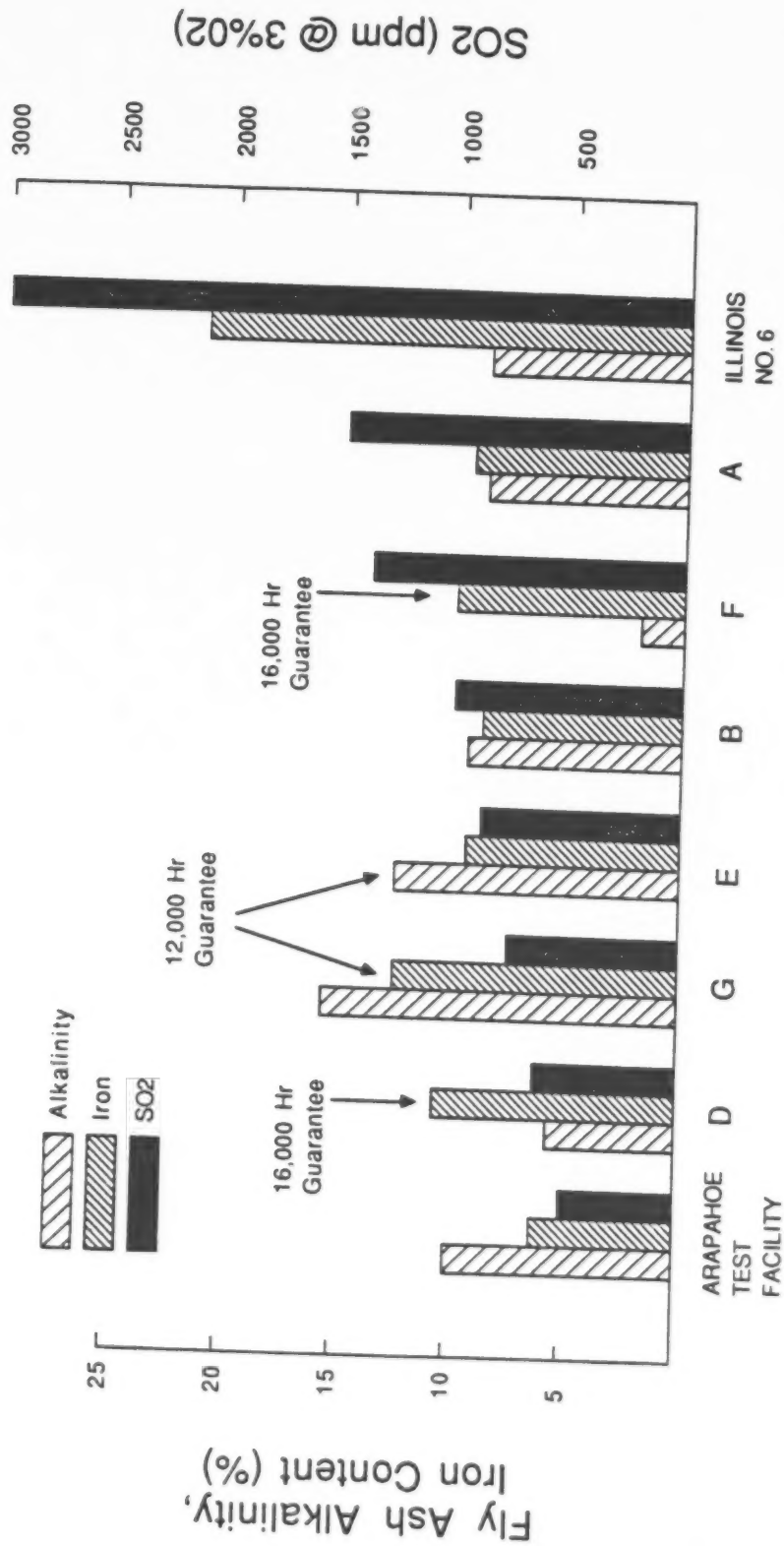


**FIGURE 5. COMPARISON OF FUELS AT EUROPEAN SCR SITES
VS. U.S. LOW AND HIGH SULFUR COALS**

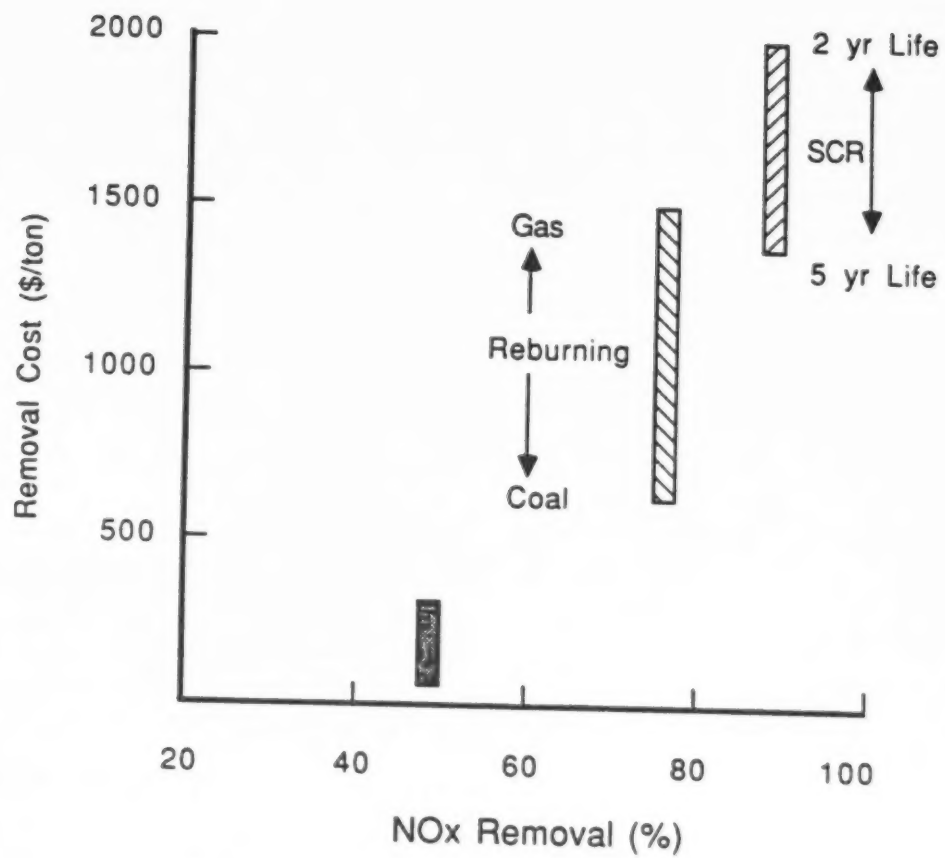


**FIGURE 6. RETROFIT NO_x CONTROL COSTS:
HIGH SULFUR COAL**

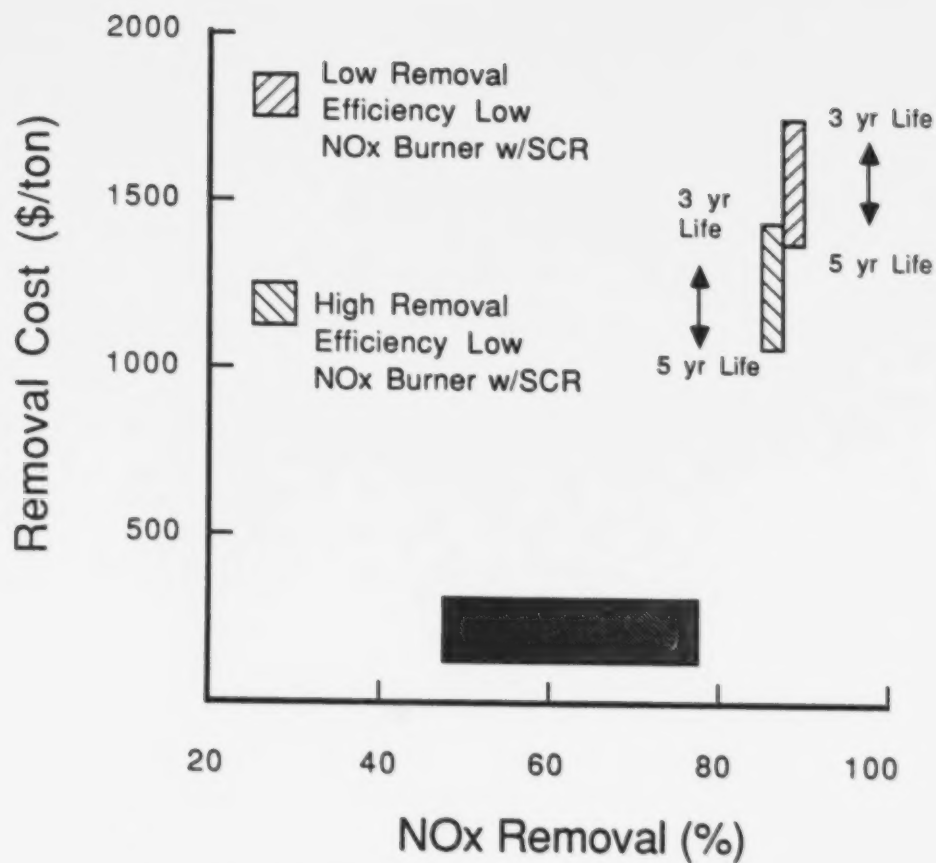


FIGURE 7. NEW PLANT NO_x CONTROL COSTS : LOW SULFUR COAL

TABLE 1. COMMERCIAL SCR SYSTEMS
IN GERMANY AND AUSTRIA⁷

<u>Utility</u>	<u>Plant</u>	<u>Capacity MW</u>	<u>Catalyst Vendor/Type</u>	<u>Start-Up</u>
Energie-Versorgung Schwaben	Heilbronn	700	EVT/ (MHI, honeycomb)	10/86
Neckarwerke	Altbach 5	420	Steinmueller (IHI, honeycomb)	11/85
NEWAG-NIOGAS/ Verbundkraft	Duernrohr No. 1,2	320, 405	Voest-Alpine Linz (Babcock-Hitachi, plate)	10/86
Technische Werke Stuttgart	Munster 15	43 [‡]	EVT (MHI, honeycomb)	8/86
VKR	Buer FWK	160 [‡]	Steinmuller (IHI, honeycomb)	late '85
VKR	Knepper C**	90	Uhde (Babcock-Hitachi, plate)	9/86
VKR	Knepper C**	90	Huls (MHI, honeycomb)	9/86

* All boilers are dry bottom units except Knepper, which is a slag tap firing system without fly ash recycle.

** Parallel systems in the same vessel, with each system treating 25% of flue gas flow.

‡ Equivalent electric capacity for combined electricity/district heating.

COMPARISON OF FOUR CATALYSTS USED IN
SELECTIVE CATALYTIC REDUCTION OF NO_x

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ABSTRACT

Tested catalysts all show a pseudo first order reaction. High activity and high specific surface is beneficial for the performance, even though high specific surface also means smaller pitch and higher pressure drop.

The operating experiences are good, with no catalyst activity deterioration.

INTRODUCTION

The need for air pollution control equipment is increasing due to an accelerated environmental stress especially in the developed world. Restricting the issue to nitrogen oxides the emitting sources are mainly power and heating plants along with automotive. The role of these varies between countries. The more heat and power that is derived from fossile fuels the larger potential for nitrogen oxide emissions. The amount that has to be reduced in each part of a country depends on the nitrogen balance for that part and the impact of exported emissions to its neighbours.

BACKGROUND

The reduction of nitrogen oxides in the flue gas can be acquired in many ways. However, only a few have the advantage of not producing any end products to be taken care of. The SCR-method (Selective Catalytic Reduction) has proven to be the most successful. This method was developed in Japan, where the so called high dust process is predominant. In this case the catalyst, with the gas flow parallel to its surfaces, is placed between the economizer and the air-preheater in the boiler. The catalyst therefore has to withstand a high dust load and minimize the SO_2 -oxidation to maintain a troublefree operation of the air preheater. If, on the other hand, the SCR-reactor is placed after the particulate- and the SO_2 -removal, narrower catalyst pitches and higher catalyst activities can be used. This so called tail end system, especially after a wet-dry SO_2 -removal system, is favourable, but not well proven. A pilot plant was therefore built at Sydkraft's power plant Öresundsverket boiler no. 15 in Malmö, Sweden.

The plant was built with support from Sydkraft AB, Statens Energi- verk, Statens Vattenfallsverk all of Sweden and Imatran Voima OY of Finland.

EPDC (Electric Power Development Company Ltd. of Japan) was consulted during the engineering and planning of the pilot, as well as for the initial ammonia and sulphur trioxide measurements.

PILOT PLANT

The flue gas, see Figure 1, first passes a Ljungström type regenerative heat exchanger. Here the gas is heated from 70°C to 300°C in an electric heater reading 350°C and then divided between two ducts, one for each reactor.

The gas flow for each reactor is measured in a venturi.

After the venturi, ammonia is introduced. The concentrated ammonia is first diluted in a smaller gas stream before it is introduced into the main gas stream. The ammonia-laden gas is passed to the reactor where it is evenly distributed over the catalyst.

The gas passes over the catalyst surfaces in the reactor, and the exhaust gas from both reactors merges in the heat exchanger where it is cooled to about 115 °C. The denitrified gas is then returned to the existing stack.

Gas flow through each reactor can be individually adjusted by means of hand-operated dampers. The total gas flow to both reactors is automatically controlled by a guide vane before the fan. Ammonia is evaporated. Heat for the evaporation is supplied in a thermostatically controlled water bath. By controlling temperature in the water bath, it is possible to control the ammonia gas pressure. A mass flow meter measures the ammonia flow to each reactor. The plant has a good thermal insulation to avoid heat losses and is well sealed to prevent leakage. The technical data of the plant are to be found in table 1.

ANALYSER SYSTEM

In the gas stream continuous analysis for water vapour, nitrogen oxide, nitrogen dioxide, oxygen and sulphur dioxide is conducted. Ammonia and sulphur trioxide are analysed from samples.

Water vapour is measured by means of an infra-red analyser, nitrogen oxide by means of an infra-red analyser and chemiluminescence, nitrogen dioxide and sulphur dioxide by means of an ultra-violet analyser and oxygen by a solid state sensor. Water vapour is measured in the raw gas with a hot analysis instrument.

Test gas is prepared from the raw gas and from the reactors. This gas first passes a particulate filter and is then cooled in a conventional test gas refrigerator. After the refrigerator a diaphragm pump transports the gas in heated lines to the control room where the analysers are located. On the reactors the gas sampling point could be freely chosen and it is possible to measure in between the catalyst layers.

In the control room a rotameter indicates the flow rate in each test gas line. An analyser can be selected from any of the three test gas lines. More than one analyser can be used on the same test gas line. This enables a comparison to be made between different analysers.

CONTROL SYSTEM

The total gas flow through the plant is automatically controlled and is independent of the boiler load. The gas flow per reactor can be varied up to 6,500 Nm³/h. The temperature in the plant is controlled by means of an electric heater and can be set at a level between 70 °C to 400 °C.

From the gas flow, the temperature, the pressure and the nitrogen oxide content, the nitrogen oxide amount is calculated. The chosen ratio of ammonia to nitrogen oxide (stoichiometry) determines the amount of ammonia to be supplied to the reactor. The stoichiometry can be varied up to 1.5.

TEST PROGRAMME

In order to determine the catalyst performance measurements with fixed as well as variable settings of gas flow, temperature and stoichiometry (NH_3/NO_x) are being made.

For each setting of gas flow, temperature and stoichiometry ammonia is sampled manually at different catalyst levels and thereafter the amount is wet chemically determined in the laboratory. This method gives an integral value and therefore a mean value from the continuous analyzers is used for comparison.

Simultaneously two catalysts can be tested, one in each reactor. During the season 1985 to 1986 two plate type catalysts were tried and during the season 1986 to 1987 one plate and one honeycomb. The aim is to find the optimum catalyst for a tail end system by varying both pitch and activity.

CATALYSTS

All tested catalysts are of parallel flow type. This means that the flue gas flows over the catalyst surface and the gas molecules are transported to and from the surface by means of diffusion. By altering the catalyst pitch and configuration the specific surface is varied and by altering the chemical composition the catalyst activity is changed.

The specific surface and the activity are the two important characterizations of a deNO_x -catalyst.

When the gas flow is increased over a fixed amount of catalyst and a fixed NH_3/NO_x -molar ratio, the ammonia slip at a certain gas flow takes off from a very low level to full break through. This point determines the area velocity at ammonia slip break through. (See figure 3.)

The catalyst activity may be characterized as

$$k = - AV_s \ln \left(1 - \frac{\eta}{S} \right) \quad (1)$$

where k = activity coefficient

$$AV_s = \frac{Q_s}{A} = \text{Area velocity at } \text{NH}_3\text{-slip break through}$$

Q_s = gas flow at NH_3 -slip break through

A_s = catalyst surface area

η = NO_x -reduction

S = stoichiometry

The activity coefficient generally increases with temperature. The slope of the change is determined by the catalyst composition.

The tested catalysts are all based on TiO_2 with V_2O_5 as the active material.

The catalyst activity increases with increasing amount of V_2O_5 , but the V_2O_5 is also an oxidation catalyst, which means oxidation of present SO_2 to SO_3 . This oxidation can be somewhat suppressed by doping the catalyst with other oxides.

The catalyst can principally be of plate- or "honey comb"-type. The "honey comb type" is an extruded element and the catalyst walls are self-supporting. The material is brittle and therefore chock sensitive. The plate type has a built in matrix of metal enabling the manufacturing of thinner catalyst walls. The matrix also gives a better chock resistance. Both types are being tried.

PRESSURE DROP

For a given gas velocity the pressure drop over the catalyst increases with decreasing pitches. But smaller pitches also give a larger specific surface. Therefore a straight forward comparison of pressure drop is not meaningful. To equalize the diffusion transport resistance for gas molecules from the bulk to the catalyst surface and vice versa a certain velocity in the catalyst channels, well in the laminar region, is chosen.

The laminar flow will minimize the particulate transport to the catalyst surface. The change from laminar to turbulent flow comes at Reynolds numbers between 1000 and 2000.

This channel velocity is converted to the bulk velocity outside the catalyst by the catalyst void fraction (ϵ).

Thus the comparable pressure drop is proportional to

$$\frac{\epsilon}{A_s}, \text{ which gives the factor } \frac{\Delta P \cdot \epsilon}{A_s}$$

where ΔP = pressure drop per gas passage length

ϵ = void fraction

A_s = catalyst specific surface

PERFORMANCE RESULTS

All catalysts tested respond with a pseudo first order reaction behavior for an increased ammonia supplement up to a certain stoichiometry. Beyond this stoichiometry the NO_x -reduction will become fixed value. Where this pseudo first order reaction behavior terminates depends on the amount of catalyst per gas flow.

Two expressions are used to describe the amount of catalyst, space velocity (SV) and area velocity (AV).

Space velocity equals the quote between gas flow and catalyst volume and area velocity the quota between gas flow and catalyst surface.

In figure 2 respond functions for the tested catalysts are shown.

The space velocity or area velocity can be varied either by changing the gas flow or the longitudinal coordinate of the flue gas passage, all according to the following formulas:

$$SV = \frac{LV}{n \cdot h} \quad (2); \quad AV = \frac{SV}{A_s} \quad (3)$$

SV = space velocity
LV = linear velocity
n = number of catalyst layers
h = height of a catalyst layer
AV = area velocity
As = catalyst specific area

The linear velocity will influence on the transport resistance for gas molecules to and from the catalyst surface. However, the Reynolds' number during our testing is generally between 200 and 2000. In this laminar flow region we have found the influence of the linear velocity on the overall reaction rate to be minor.

The catalyst activity as defined by equation 1 is compared in table 2. Here also pitch and specific surface are shown.

Catalysts C and D are showing the same activity after 1500 hours of operation. Catalysts A and B has been in operation only 600 hours, but also show no activity deterioration.

The very high NO_x-reduction capability for the different catalysts presented here is the result of a precise ammonia-mixing in the flue gas over the catalyst.

This will of course not be possible in a large commercial plant.

The sulphurtrioxide concentration in the flue gas to the catalysts was during the testing of catalyst C and D about 1 ppm or about 1 % of the sulphur dioxide concentration. The oxidation of sulphur dioxide was 0.5 - 1 %. During the testing of catalysts A and B however the inlet sulphurtrioxid concentration is 3 - 4 % of the sulphurdioxide concentration and the oxidation about 2 - 4 %. The relatively short operating period (600 hours) has not shown any influence on operation and performance.

The pressure drop as defined by equation 4 is compared in table 3.

The channel velocity 6 m/s is chosen to have all comparing catalysts in the laminar flow region. The corresponding Reynolds' numbers in this case varied between 300 and 800.

The costs for the increased pressure drop when using catalysts with higher specific surface must be evaluated from case to case.

The height of a catalyst layer is a discrete step generally 0.5 - 1 m. For a fixed area velocity this will give more "spare catalyst" with increasing specific surface.

OPERATING EXPERIENCES

The operating experiences with the whole pilot plant are good.

The heat exchanger has operated without any cleaning since the start up 1985.

By measuring the sulphurtrioxide and the ammonia in and out of the heat exchanger it has been shown that the molar ratio between NH_3 and SO_3 is in favour for the formation of ammonia sulphate instead of ammoniabisulphate. Ammonia sulphate sublimates in the heat exchanger and will therefore to the greater extent pass with the flue gases.

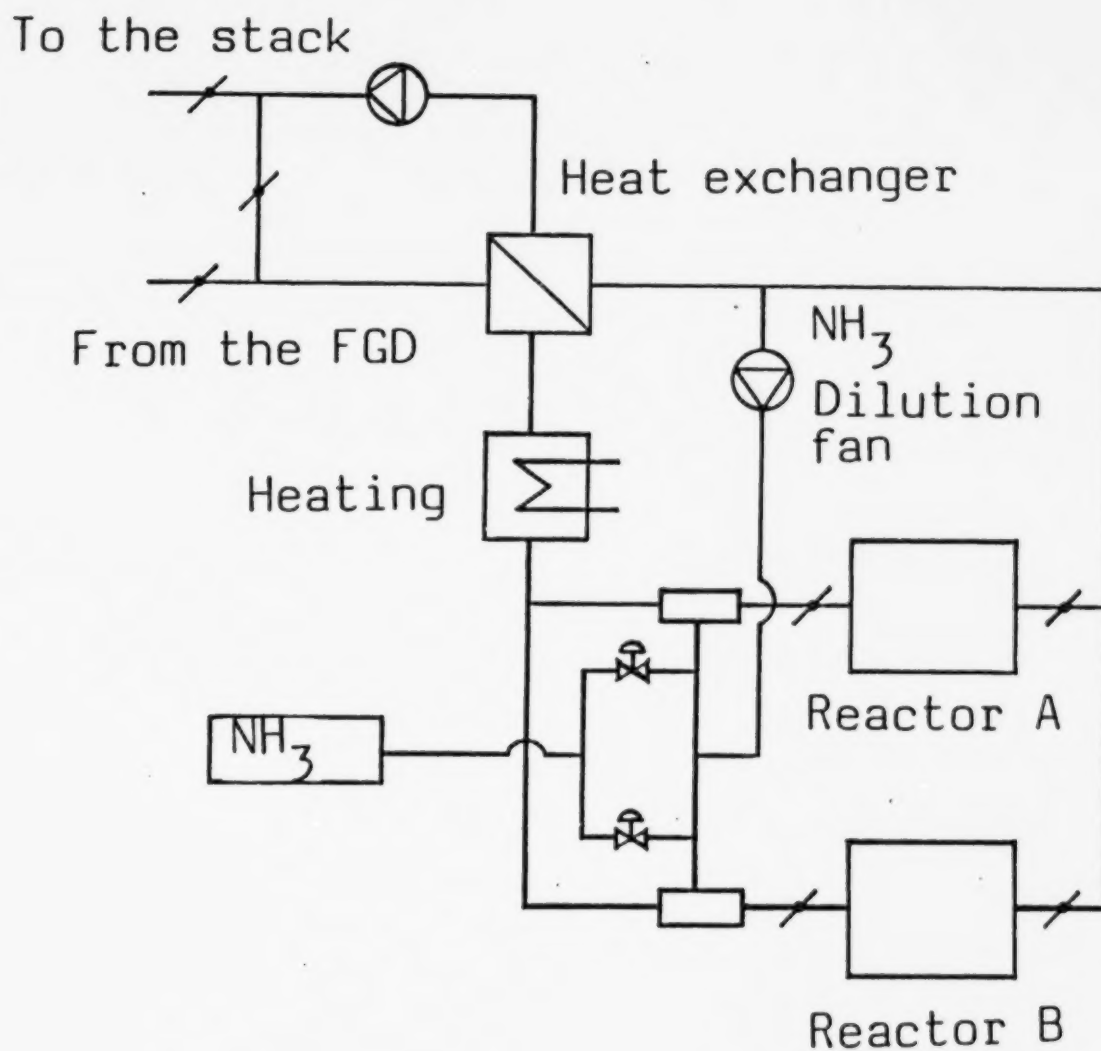
Ammoniabisulphate on the other hand is a corrosive liquid that will condensate, between 220 - 280 °C depending on the partial pressures, and stick to the heat exchanger surfaces.

The pressure drop over the heat-exchanger has increased very little, even during a period last year when a lot of particulates passed the bag filter enclosed in the FGD-plant. This increased particulate load also did not harm the catalyst performance.

The gas ducts are made of mild steel and the iron oxides upon the surface is initially catalytic active. This made it difficult to measure the catalysts denitrification during the first couple of hundred hours.

The analysers are all working well with normal maintenance and are calibrated once a day with calibration gas. The chemiluminiscence instrument shows the largest drift and has determined the calibration intervals.

DeNO_x Pilot Plant, Malmö Sweden



Flow diagram

Fig. 1

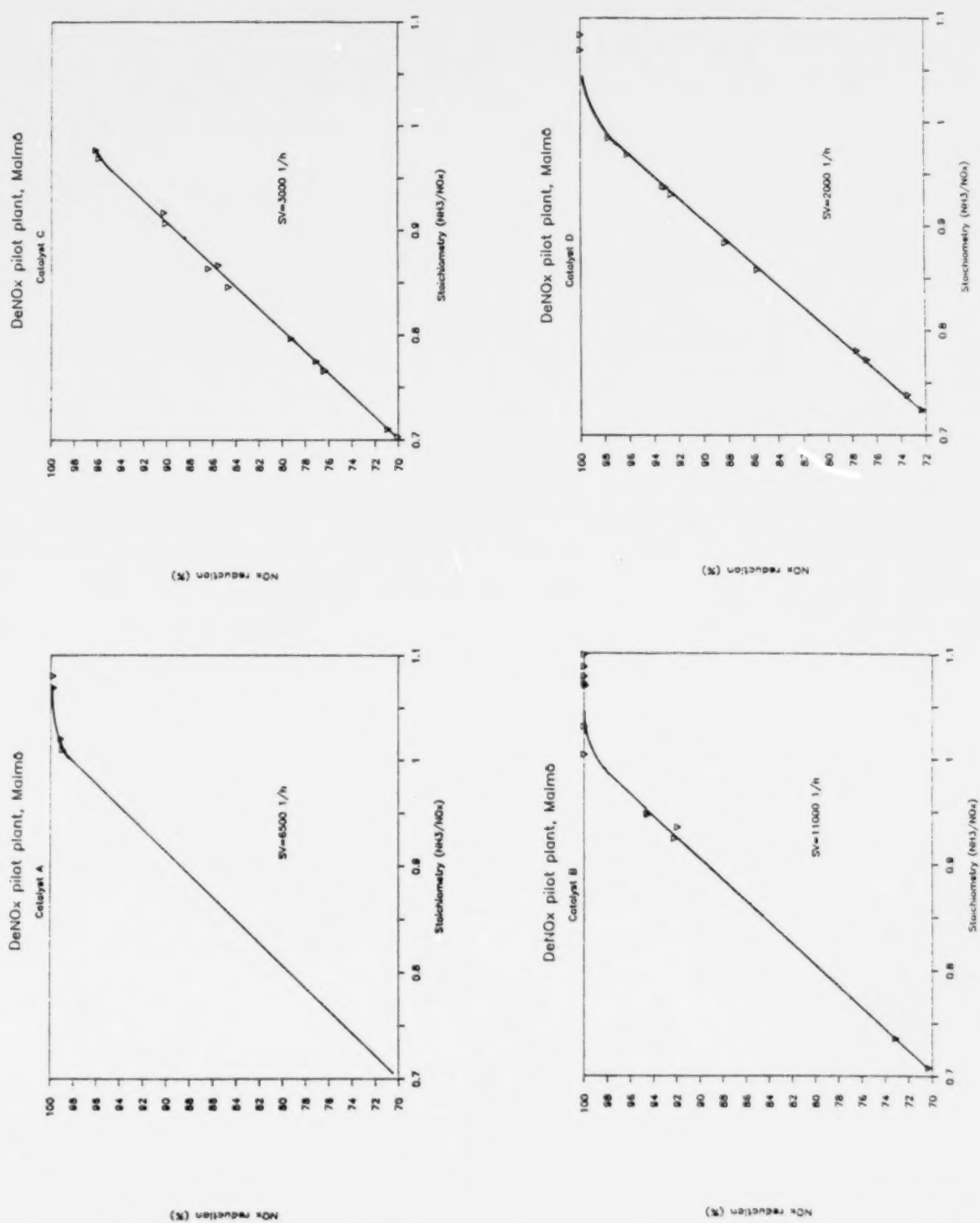


Fig. 2

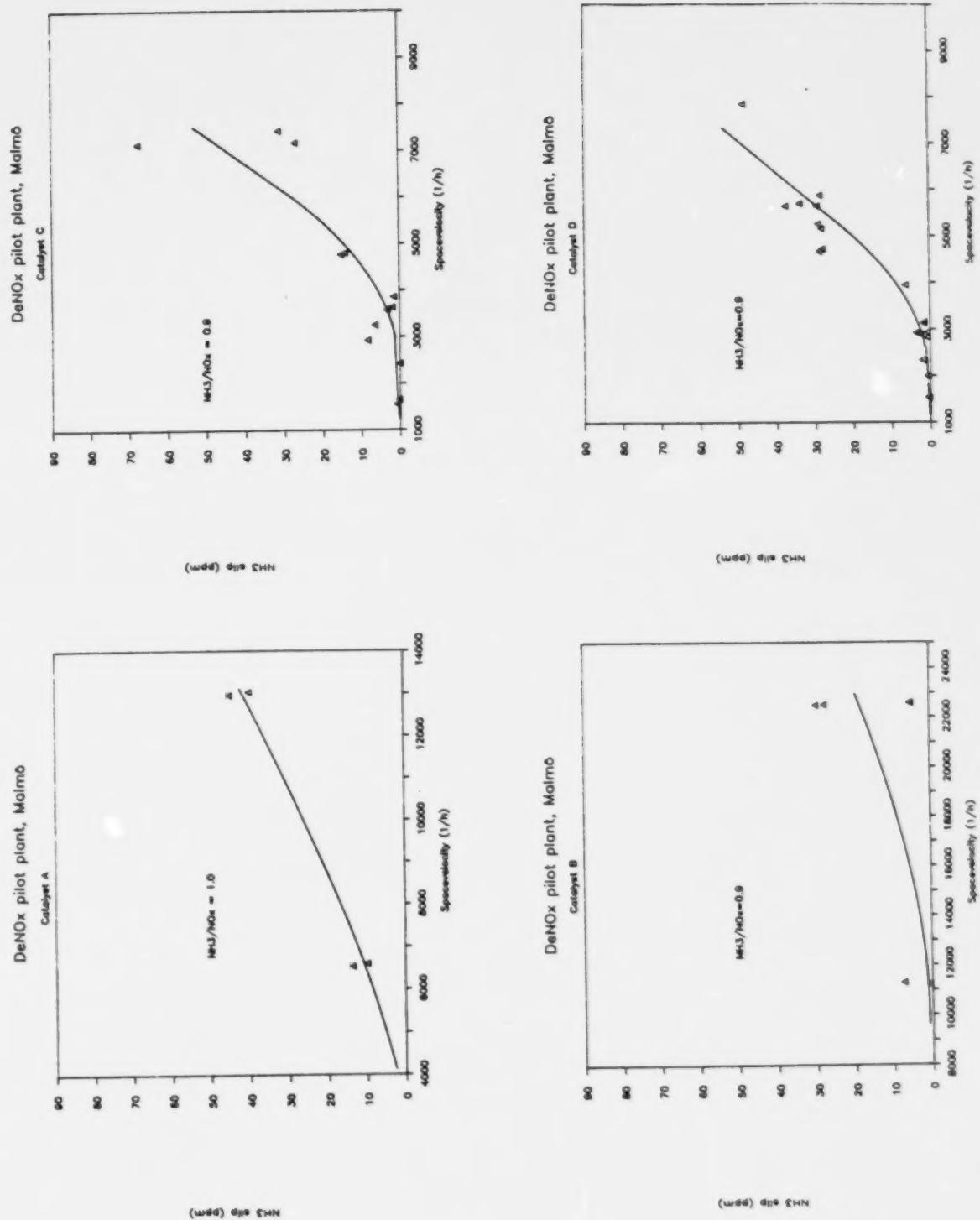


Fig. 3.

TABLE 1. PILOT PLANT DATA

Reactors in parallel		2
Nominal gas flow per reactor	Nm ³ /h	5000
Normal operating temperature	°C	350
NO _x inlet concentration (6 % O ₂)	ppm	600
SO ₂ " - (6 % O ₂)	ppm	100
SO ₃ " - (6 % O ₂)	ppm	1 - 3
Particulates (6 % O ₂)	mg/Nm ³	2

TABLE 2. CATALYST COMPARISON

Type	Pitch (mm)	A _s (%)	k (%)	Kind
A	4	79	38	Honeycomb
B	3	100	100	Plate
C	6	38	52	Plate
D	10	47	28.3	Plate

TABLE 3. PRESSURE DROP COMPARISON.

Type	V _c (m/s)	$\frac{\Delta P \cdot \epsilon}{A_s}$ (%)
A	6	100
B	6	53
C	6	30
D	6	24

THE IMPROVEMENT OF NH₃ INJECTION CONTROL SYSTEM FOR A SELECTIVE
CATALYTIC NO_x REMOVAL SYSTEM

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ABSTRACT

Mitsubishi Heavy Industries has supplied the Selective Catalytic NO_x Removal system (SCR system) of more than 90 units both in Japan and abroad since it delivered the first SCR system for a boiler in 1976. This paper describes the control system of a SCR system developed with a new concept to cope with the recent trend to operate a thermal power plant as a load swing operation unit and its service results in a 600 MW boiler.

INTRODUCTION

Thermal power plants, especially oil and LNG firing power plants, were orientated to large capacity and high efficiency in the high economic growth days from late 1960's to early 1970's. The policy of electric power development, however, was changed to diversification of electric power sources by two oil embargoes in 1973 and 1979. Development of electric power generation by nuclear energies and other energies substituting oil energies was promoted positively.

Table 1*1 shows the plan of electric power source proportion in the interim report prepared by the Supply and Demand Committee of Electricity Utility Industry Council, Agency of Natural Resources and Energy, Ministry of International Trade and Industry, Japan. The ratio of nuclear power generation will be increased steadily and the role of fossile-fuel power generation will be increasingly shifted from base load operation to middle and load swing operation.

Mitsubishi Heavy Industries, Ltd. (MHI) has delivered more than 90 selective catalytic NO_x removal systems (SCR) to domestic and overseas customers as shown in Table 2 since 1976 when we delivered SCRs for boilers. We, however, have drawn up a project for improving the control system of SCR according to the above-mentioned change in the operation status of thermal power plants so that SCR can follow the rapid fluctuation of load.

Being outlined is the description of a new SCR control system newly developed under the project and the results of tests carried out on the control system in a large capacity 600 MW plant.

NEW SCR CONTROL SYSTEM

Problems in Conventional Control Systems

The control method of nitrogen oxides emitted from the plant is compelled to change according to the recent great change in the operation of fossil fuel power plants. Conventional nitrogen oxide control methods are designed by considering the base load operation of plants and an amount of NH_3 required by SCR is determined according to NO_x concentration and fuel flow rate as shown in Fig. 1. Outlet NO_x concentration exceeds a given level at the initial parameter setting for any reason such as aging, bias to the NH_3/NO_x mol ratio is adjusted manually for diminishing the concentration below the given level.

The simple control method based on static characteristics can fulfil the requirement satisfactorily for base load operation. The inlet conditions of SCR, however, are changed as stated below as the operation of the plant is shifted to load swing operation.

In load swing operation, the load fluctuation frequency is high and the degree is great in comparison with base load operation. Accordingly the fluctuation of emission gas flow rate is rapid and extensive. NO_x concentration at the outlet of the economizer also varies drastically. Further gas temperature at the outlet of the economizer fluctuates more less.

Fig. 2 shows fluctuation in SCR inlet NO_x concentration, gas flow rate, gas temperature, and oxygen concentration, brought about by load fluctuation. Fig. 2 shows the variation of conditions at the inlet of SCR when the load was altered from 3/4 to 4/4 at a rate of 6 %/min. At the time, NO_x concentration from 29 ppm to 55 ppm and then diminished to 34 ppm.

The control logic shown in Fig. 1 reveals that the flow rate of adding NH_3 rises with the increase of NO_x concentration at the inlet of SCR. A problem, however, is that the time constant of NO_x removal reaction is very large.

Fig. 3 shows the response of NO_x concentration at the outlet of SCR to the variation of NH_3 flow rate step with NO_x concentration at the inlet of SCR constant. The time constant of NO_x concentration at the outlet of SCR is about 10 to 12 minutes for step of NH_3 flow rate. On conventional static characteristic based control systems, the parameters are set for an NO_x concentration at the outlet of economizer stabilized after fluctuation, and the system is not so designed as to regulate concentrations such as 55 ppm in Fig. 2 during fluctuation.

If the NH_3 flow rate is set against the rapid fluctuation of NO_x concentration at the outlet of the economizer, the flow rate of NH_3 will be in excess for the NO_x concentration at the outlet of the economizer when the load is settled. As a result, NH_3 concentration in the flue gas at the inlet of the stack will exceed the control level.

If the plant is operated primarily for the base load, it is possible to adjust the NH_3 rate before changing the load and again adjust the rate to an optimum level after the load is settled.

In swing load operation, however, the frequency of load change is very high and manual regulation according to load variation is nearly impossible especially under AFC (Automatic Frequency Control) operation, tending to feed NH_3 in excess for regulating NO_x concentration at the outlet of SCR.

A new control logic combining feed-forward control and feed-back control adequately has been developed for solving the above problems.

NOx Removal Reaction Model

Difficulty in NOx control is that the time constant from the variation of ammonia flow rate to SCR to the corresponding variation of outlet NOx concentration is very long as shown in Fig. 3. Namely, outlet NOx concentration is not changed immediately after the addition of ammonia. Consequently adoption of feed-back control is difficult and the employment of a control logic close to the simple open loop like the conventional control system is compelled.

To solve the problem, we developed a method in which a mathematical model of an NOx removal reaction is integrated into the control system and an adequate NH₃ flow rate is determined according to the results of real time simulation carried out by the model. Fig. 4 shows the SCR reaction model by the method.

The precondition for embodying the above method to the control system is the adoption of digital equipment and not analog modules. The method is realized by recent rapidly speeded up process and reduced prices of digital computer.

The following basic equation is acquired from the mass balance of NH₃ adsorbed to the surface of catalyst.

$$W \frac{dQ}{dt} = V_S - V_L - V_R \text{ ----- (1)}$$

where Q : amount of NH₃ adsorbed by catalyst (Nm³/m³ - catalyst)
 W : volume of filled catalyst (m³)
 V_S : amount of fed NH₃ (Nm³/H)
 V_L : amount of NH₃ separated from catalyst (Nm³/H)
 V_R : amount of NH₃ consumed by reaction with NOx (Nm³/H)

It is possible to predict the outlet NOx concentration and NH₃ concentration of SCR from the above equation based on NH₃ adsorption, reaction speed, etc. of the catalyst acquired by experiments. Fig. 5 shows the results of simulation by the equation. The results may be different from absolute values more or less but the tendency and timing are presumably agree with the actual conditions.

Considerable deviations in absolute values can be prevented by making the initial values agree with measurements at every sampling carried out at given regular intervals. Thus the real time simulation model shown in Fig. 5 can be used for practical control.

New Control Logic

The new control logic which is being outlined is an adequate combination of feed-back control and feed-forward control with a core of the NOx removing reaction model for improving in the shortcomings of the conventional logic. The final flow rate of NH₃ is the sum of the following five values.

(1) NH₃ Flow Rate Determined from Mass Balance B₁

When the load is settled, the flow rate of flue gas is determined by the load and the NOx concentration in the flue gas is also determined by the load. Accordingly the required NH₃ flow rate is expressed as a function of the load.

More rapid response the conventional control method is expectable by employing the load demand instead of the fuel flow rate.

$B_1 \leftarrow FX \text{ (MWD)}$ MWD : load demand

(2) Control against Load Increase B_2

More energies than those output from the plant must be input transitionally when the load is increased as the overall energy level of the plant is raised from low to high level.

The control is carried out by APC (Automatic Plant Control), the controller of the boiler. On SCR, however, NH_3 in larger amount than that B_1 determined from mass balance must be fed transitionally in accordance with the characteristic of the upstream system at load raising.

When the load is reduced, fuel is diminished and NH_3 in smaller amount than B_1 should be fed. This, however, needs not be considered from a standpoint of regulating the SCR outlet NO_x concentration to below a given level. Only the measure for load increase must be taken into consideration.

B_2 output logic is:

- a. NH_3 is added pulsatively when the load is raised.
- b. Pulse intensity is variable according to the load range.
- c. Pulse width is variable according to the load range.
- d. Pulse output is stopped on the spot if the load demand declines before completing pulse output.
- e. If stack inlet NH_3 concentration is high, feed of NH_3 is stopped on an assumption that enough amount of NH_3 is in SCR reactor. Output is stopped also when stack inlet NO_x concentration is very low.

(3) Control against Inlet NO_x Concentration of Stack B_3

An NH_3 feed signal is output according to the following logic when the outlet NO_x concentration can not be regulated below a given level by B_1 and B_2 .

$$\begin{aligned} \Delta NX &\leftarrow NX_{OUT} - NX_{OUT} - SET \\ B_3 &\leftarrow \alpha_1 \text{ at } \Delta NX > \epsilon_1 \\ B_3 &\leftarrow 0 \text{ at } \Delta NX < \epsilon_2 \\ &(\epsilon_1 > \epsilon_2) \end{aligned}$$

where NX_{out} : predicted SCR outlet NO_x concentration (obtained by simulated calculation)

$NX_{out-set}$: set point of SCR outlet NO_x concentration

The above logic uses the accessed SCR NO_x concentration by real time simulation and not the measured concentration. The variation of SCR outlet NO_x concentration is predicted before the concentration is changed by the change of SCR inlet NO_x concentration or gas temperature. Whereby, increase of SCR outlet NO_x concentration can be prevented.

(4) Residual NH₃ Control (1) B₄

If NH₃ flow rate is raised by B₂ and B₃ against rapid SCR outlet NO_x concentration rise by load increase, the residual NH₃ concentration may be increased when load variation is ended or load is declined abruptly. To prevent this, the NH₃ flow rate is adjusted according to the following logic.

$$\begin{array}{ll} \Delta \text{NH} & \leftarrow \text{NH}_{\text{OUT}} - \text{NH}_{\text{OUT-SET}} \\ B_4 & \leftarrow -\alpha_2 (\alpha_2 > 0) \quad \text{at } \Delta \text{NH} > \epsilon_3 \\ B_4 & \leftarrow 0 \quad \text{at } \Delta \text{NH} < \epsilon_4 \end{array}$$

where NH_{out} : measured SCR outlet NH₃ concentration
NH_{out-set} : set point of SCR outlet NH₃ concentration

Control of residual NH₃ concentration by B₄ is an urgent control and is usually made by the following B₅.

(5) Residual NN₃ Control (2) B₅

Residual NH₃ concentration inevitably tends to be high when SCR outlet NO_x concentration is controlled to below a given level. To avoid this trend, a proportional-integral (PI) controller shown in Fig. 6 is used. The PI controller is arranged for making the predicted SCR outlet NH₃ concentration acquired by simulation agree with a certain reference value (set point). The use of the predicted value instead of measurement prevents offset even if the reset ratio of the PI controller is set high more or less, permitting to avoid SCR outlet NO_x concentration from exceeding a given control level by excessive reduction of the NH₃ flow rate.

The new control logic determines the final NH₃ flow rate by adding all B₁, B₂, B₃, B₄, and B₅.

RESULTS OF APPLICATION

The SCR control system outlined so far was experimentally applied to an LNG firing 600 MW boiler in December, 1985. Since then, this system has shown satisfactory control characteristic, proving its efficiency.

The overall layout of the plant and the outline diagram of the SCR reactor are shown in Figs. 7-1 and 7-2. The major specifications of the boiler and SCR reactor are shown in Table 3.

The plant is primarily operated for the peak load and the load is varied extensively from time to time. At plants of frequent load variations, NH₃ is usually fed in excess for controlling SCR outlet NO_x concentration to below a given level. By the employment of the new control system, the feeding rate of NH₃ is kept to an optimum level and residual NH₃ concentration is reduced. Figs. 8 to 11 show the examples of control by conventional and new control system.

CONCLUSION

MHI begins the development of SCR for boilers around 1973 and has continued efforts for developing the technology ever since.

Development of catalyst shape, composition, manufacturing method, and others adequate for boiler flue gas characteristics has been promoted, and a system capable of supplying high performance, long life catalysts has been established. Required for improving SCR in reliability are overall studies on the structure, control logic, and others. The control system capable of adjusting according to the variation of load, developed based on our studies, has been introduced together with its application data.

The operation styles of fossil-fuel power stations will be increasingly diversified and we will continue our efforts for improving SCR including catalysts and control logic to meet the demand.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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p.27 to p.28 Vol. 37 No. 353, (FEB. 1986)

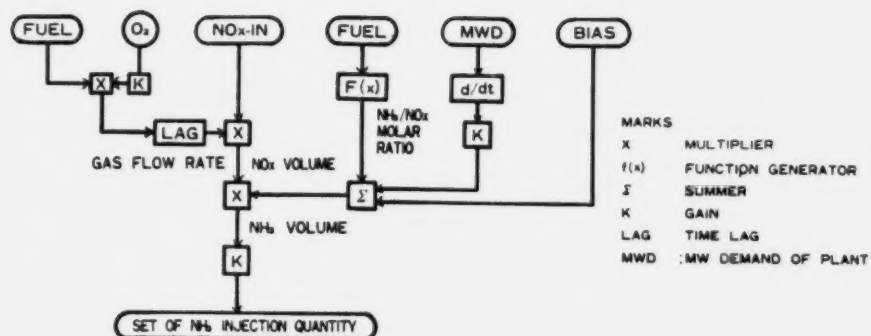


Figure 1. Logic of present control system

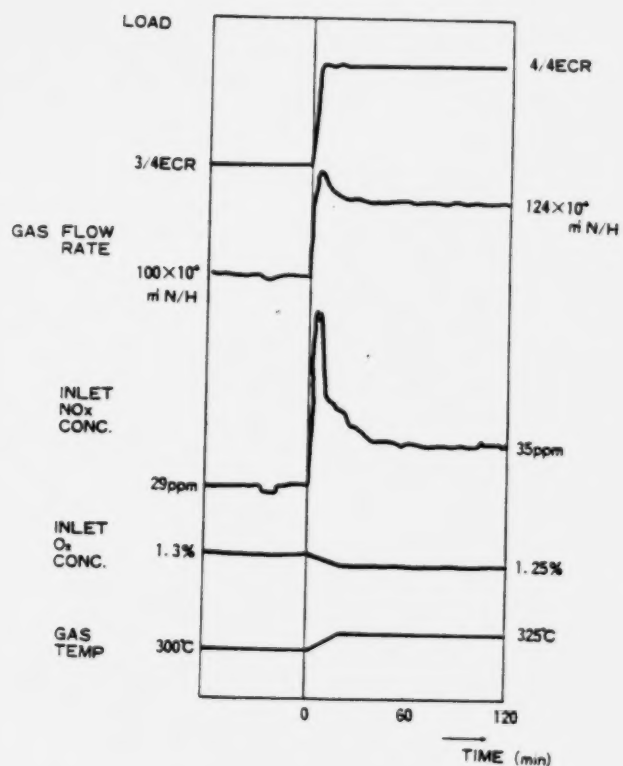


Figure 2. Variation of SCR inlet gas condition at load change

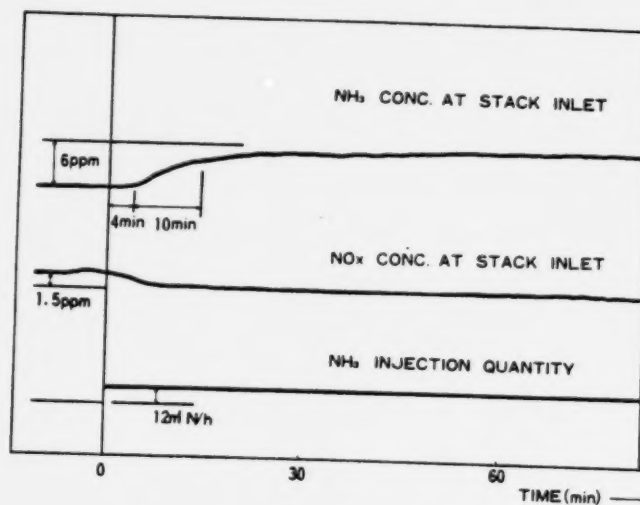


Figure 3. Variation test of NH_3 injection quantity

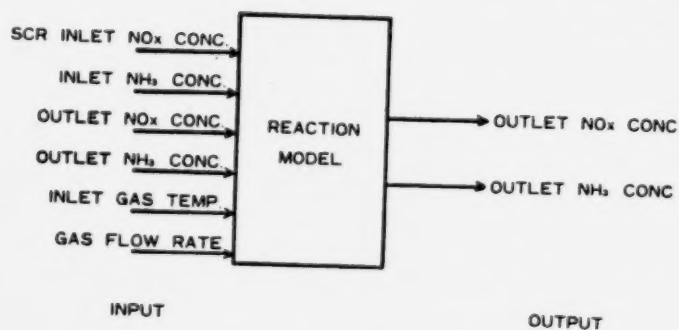


Figure 4. SCR reaction model

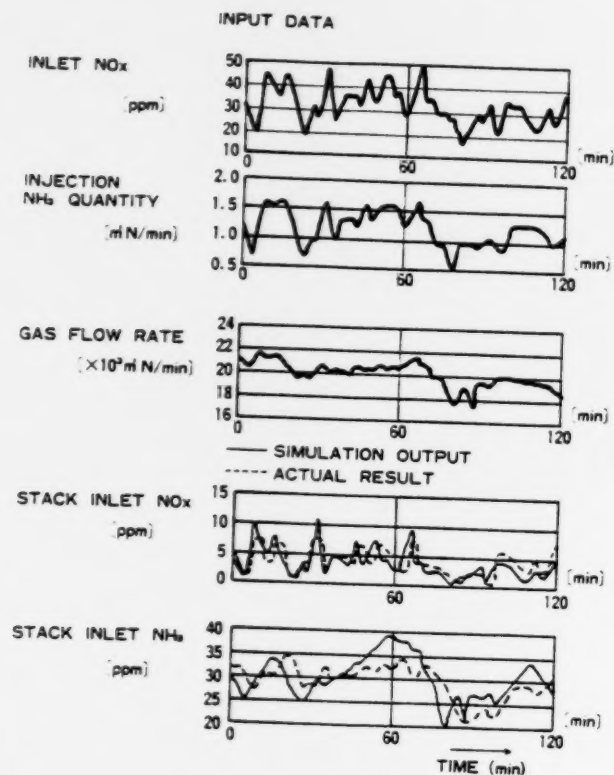


Figure 5. Simulation result

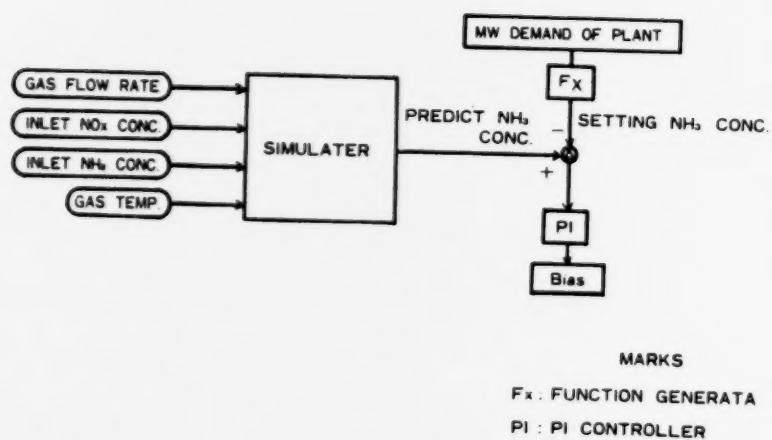


Figure 6. Control system of NH₃ conc. at SCR outlet

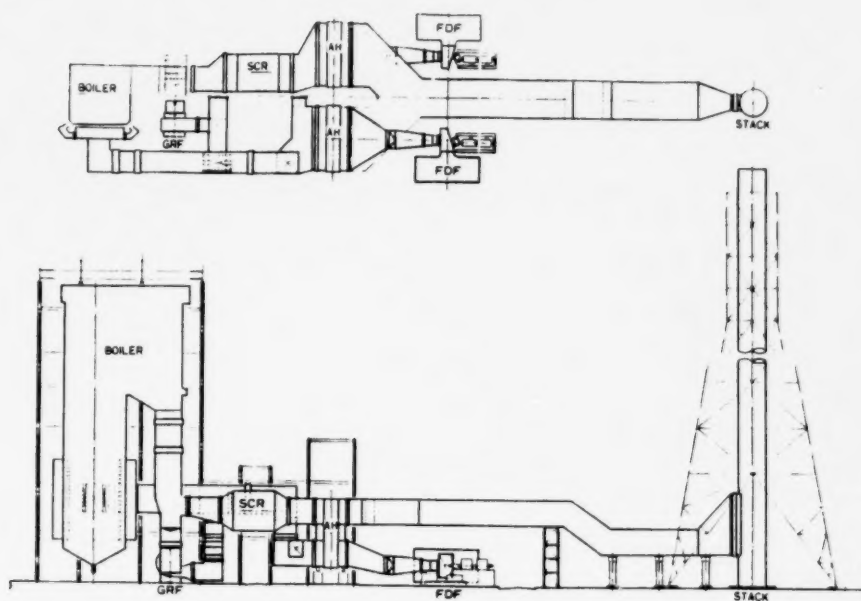


Figure 7-1. Total arrangement of 600 MW LNG firing plant

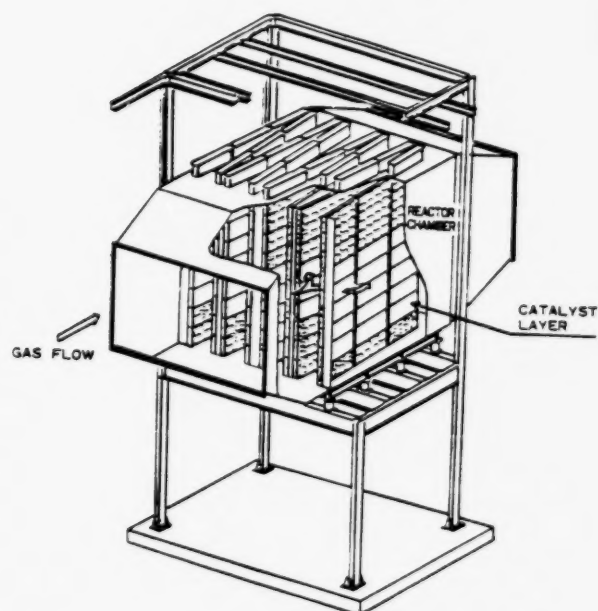


Figure 7-2. Bird's-eye view of SCR reactor

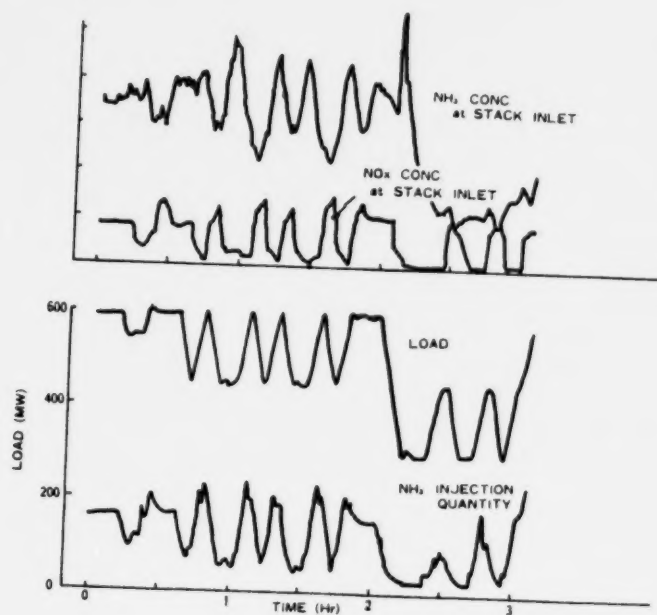


Figure 8. Actual control result at change of boiler load (by old control system)

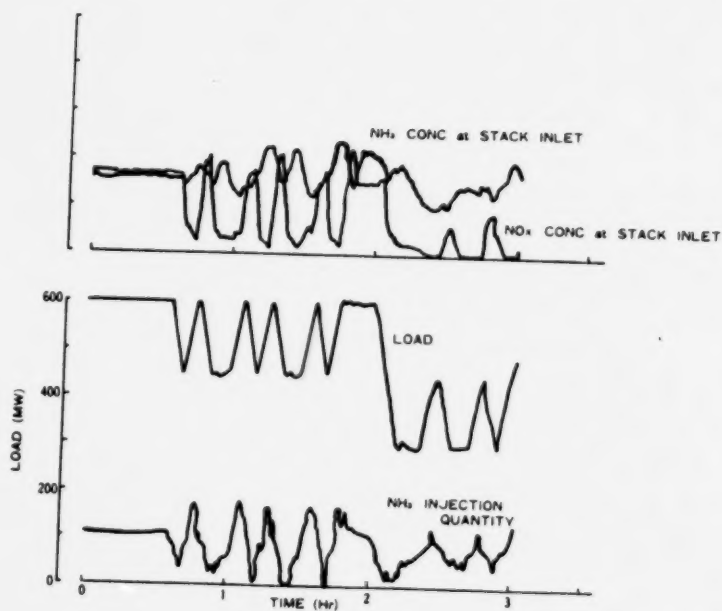


Figure 9. Actual control result at load change (by new control system)

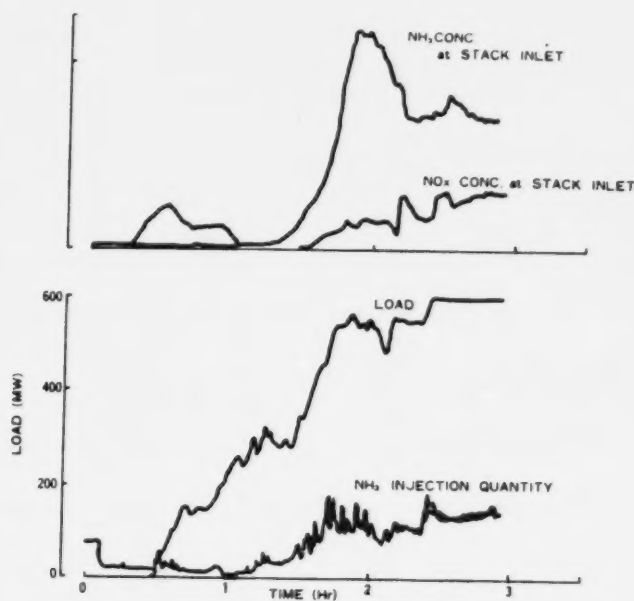


Figure 10. Actual control result at start of boiler
(by old control system)

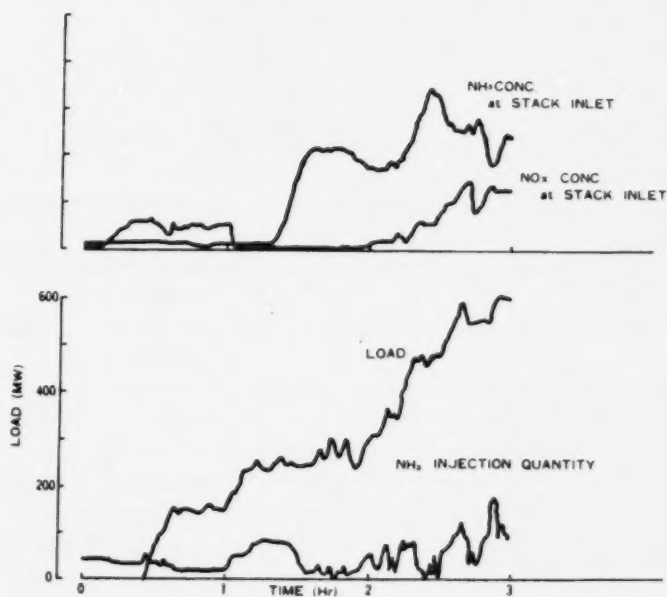


Figure 11. Actual control result at start of boiler
(by new control system)

Table 1. Plan of electric power source proportion
(interim report by Electricity Utility
Industry Council, Agency)

	ELECTRIC POWER PLANT ($\times 10^4$ KW)							
	1982		1990		1995		2000 (calculation)	
		Proportion (%)		Proportion (%)		Proportion (%)		Proportion (%)
NUCLEAR	1,718	12.3	3,400	19.0	4,800	23.0	about 6,200	27.0
COAL	665	4.8	1,400	8.0	2,100	10.0	about 3,000	13.0
LNG	2,021	14.5	4,000	23.0	4,350	21.0	about 4,350	19.0
HYDRAULIC	3,219	23.0	33,850	22.0	4,200	21.0	about 4,650	20.0
GEOTHERMAL	18	0.1	60	0.3	150	0.7	about 300	1.0
OIL-LNG	6,343	45.3	5,000	28.0	4,900	24.0	about 4,700	20.0
TOTAL	13,984	100.0	17,710	100.0	20,500	100.0	about 23,200	100.0

Table 2. Supply record status on system

(As of March, 1987)

FIELD		FUEL	GAS	OIL	COAL (COAL/OIL)	NUMBER OF UNIT
DOMESTIC	UTILITY		10	33	13	56
	INDUSTRIAL		8	9	3	17
OVERSEAS	UTILITY		1	2	8	11
CUSTOMERS	INDUSTRIAL		6	-	-	3
NUMBER OF UNIT			25	44	24	93

Table 3. Specification of 600 MW LNG firing plant

EQUIPMENT	SPECIFICATION
BOILER	TYPE: MITSUBISHI SULZER MONO-TUBE, VARIABLE SUPER CRITICAL PRESSURE BOILER MAXIMUM CONTINUOUS STEAM GENERATION: 1950 TON/HR MAXIMUM OPERATING PRESSURE(SUPERHEATER/REHEATER) 255/56 kg/cm² STEAM TEMPERATURE(SUPERHEATER OUTLET/REHEATER OUTLET) 543/569 °C
SCR	METHOD: SELECTIVE CATALYTIC NOX REMOVAL SYSTEM REACTOR TYPE: HORIZONTAL FLOW, FIXED BED TYPE (PELLET CATALYST) NO. OF REACTORS: TWO SETS/BOILER EFFICIENCY: 810,000 m³/HR SET GAS TEMPERATURE: 340°C (MCR) OUTLET NOX CONCENTRATION: 10 PPM OUTLET NH₃ CONCENTRATION: 10 PPM

DEVELOPMENT OF LOW LEVEL NH₃ MEASURING METHOD

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ABSTRACT

Performance of NO_x reducing catalyst shall be continuously checked by measuring slip NH₃ at the downstream of SCR reactor.

There are two different methods to measure low level NH₃, so-called a direct method and an indirect method. An indirect method has to use a catalyst, which is the same kind of what we are going to check the performance, in order to convert NH₃ to NO.

EPDC and Anritsu Corporation developed jointly the direct NH₃ measurement and applied it at Takehara #3 (700MW) unit.

This instrument detects ultraviolet absorption of NH₃ spectrum by frequency modulation.

Sampling method is also important to measure low level NH₃ (0-20 ppm) and is developed by us. This paper will describe the principle of these methods.

1. Introduction

For the stable operation of the de-NO_x equipment of ammonium selective catalytic reduction method for coal fired power plants, it is essential to control the performance of the catalyst. The catalyst deterioration must carefully be monitored, for example, and it is necessary, for this purpose, to accurately and consistently measure the low level residual ammonia of a few ppm.

Many ammonia analyzers have been developed for the purpose of such continuous monitoring. The methods include, for example, the solution conductivity method, microwave absorption method⁽¹⁾, infrared absorption method, catalytic oxidation method⁽²⁾, catalytic reduction method⁽²⁾ and ultraviolet absorption method⁽³⁾. The catalytic oxidation method oxidizes NH₃ into NO_x and measures NO_x with an NO_x analyzer. The catalytic reduction method on the other hand denitrifies using denitrification catalyst and measures the decrease of NO_x with a NO_x analyzer to determine the NH₃ concentration. Ammonia analyzers in practical use now employ the

catalytic reduction method or the ultraviolet absorption method, and analyzers which use other methods are not in use now because of their disadvantages.

Anritsu Corporation has developed a direct method ammonia analyzer of ultraviolet spectroscopy that in principle satisfies the required accuracy. This feature called the attention of Electric Power Development Co., Ltd., and a joint demonstration was carried out for the period of from February 1982 to February 1983. The test revealed that the ammonia analyzer is satisfactory with some improvements^{(4),(5)}, and an ammonia analyzer of this type was installed to EPDC's Takehara #3 unit in March 1984.

To apply the conventional catalytic reduction method (indirect method) to de-NO_x equipment is rather contradictory because it monitors deterioration of catalyst in the de-NO_x equipment with an analyzer which also suffers same kind of deterioration. If the catalyst of the analyzer deteriorates unnoticed in the course of monitoring, increase of residual ammonia in flue gas may not be noticeable. In order to avoid this to happen, it has been necessary to develop an analyzer which directly measures ammonia.

This paper describes the direct ultraviolet ammonia analyzer, and compares it with an indirect ammonia analyzer.

EPDC noticed that the measured values depend on the sampling method. Measurements were repeated with different tube temperatures and materials. It was found that the response is slow when the tube temperature is low because of NH₃ mist occurring in the tube and that some tube materials act as catalyst turning NH₃ into acid ammonium sulfate, which causes an error in the measurement.

EPDC developed a method, through these tests, where stainless steel SUS 304 is used as tube material and the tube temperature is maintained at 330°C or higher.

The sampling method is also described in this paper.

2. Principles of Measurement

2.1 Principle

The ultraviolet absorption spectrum of ammonia has a fine structure shown in Figure 1(6). An ultraviolet light which passes through NH₃ gas therefore shows a transmission spectrum of Figure 2(a). When an wavelength modulation of angular frequency ω is applied at a wavelength corresponding to an absorption peak such as that indicated by a dotted circle in Figure 2(a), as shown in Figure 2(b), an intensity-modulated signal of angular frequency 2ω is obtained as shown in Figure 2(c). The amplitude of the intensity-modulated signal is proportional to the depth of the valley in the transmission spectrum (that is, proportional to the difference between the maximum and minimum in the transmission intensity). The depth of the valley is proportional to the gas concentration when the concentration is low, and the gas concentration can be obtained by measuring the amplitude of the intensity-modulated signal.

The principle stated above is expressed mathematically below.

Assume that the intensity-modulated signal is $P(t)$. Then, in reference to Figure 2(c), $P(t)$ is expressed as

$$P(t) = P_0(1 + m \cdot \cos 2\omega t) \quad \dots (1)$$

where,

$$P_0 = \frac{I(\lambda_0) + I(\lambda_1)}{2} \quad \dots\dots (2)$$

$$m = \frac{A}{I(\lambda_0) + I(\lambda_1)} \quad \dots\dots (3)$$

($I(\lambda_1)=I(\lambda_2)$ is assumed for simplicity.)

According to the Lambert-Beer law, the transmission intensity, $I(\lambda)$ is given as follows:

$$\begin{aligned} I(\lambda) &= I_0 \cdot e^{-\sigma(\lambda) \cdot n \cdot \ell} \\ &\approx I_0 (1 - \sigma(\lambda) \cdot n \cdot \ell) \quad \dots\dots (4) \end{aligned}$$

where, $\sigma(\lambda)$ is the absorption cross section of molecule, n is the molecular density and ℓ is the absorption optical path, and the approximation given above holds when $\sigma \cdot n \cdot \ell \ll 1$. The approximation applies to our case where we are interested in ultraviolet absorption in a gas of low concentration.

From Eqs. (3) and (4),

$$m \approx \frac{\sigma(\lambda_0) - \sigma(\lambda_1)}{2} \cdot n \cdot \ell \quad \dots\dots (5)$$

The value of m therefore does not depend on the incident intensity I_0 , and is proportional only to the gas concentration (molecular density n). As seen in Eq. (3), m is the depth of valley (difference between maximum and minimum of transmission light) divided by the mean intensity of transmission light P_0 . That is, amplitude A of alternating signal of frequency 2ω and direct component P_0 are obtained from intensity-modulated signal $P(t)$, and the gas concentration is obtained from the ratio of A and P_0 .

As seen from discussions given above, this method is superior in measurement stability not affected by fluctuations in the light source or stains in the optical system.

This ammonia analyzer uses the measurement wavelength λ_0 of 209 nm and wavelength modulation width $\Delta\lambda$ ($=\lambda_2-\lambda_1$) of 3.2 nm.

2.2 Interference from Other Substances and Removal of Interference

This method does not depend on the intensity of light, and is rather insusceptible even when absorption peaks of other substances are in the same region. All the more, the measurement wavelength (209 nm) and the wavelength modulation width (3.2 nm) are conditions employed to minimize interferences from NO_x and SO_2 . When the SO_2 concentration is very high ($[\text{SO}_2] > 100$ ppm), the interference from SO_2 is not ignorable.

Figure 3 shows the absorption spectrum of SO_2 (6). The absorption cross section of SO_2 at 209 nm ($40 \times 10^{-19} \text{ cm}^2$) is almost the same as that of NH_3 . The SO_2 concentration in flue gas is extremely greater than that of leak ammonia to be measured. When the concentration of leak ammonia is 5 ppm and the SO_2 concentration is 1,000 ppm, for example, the absorbance ratio, $A_{\text{SO}_2}/A_{\text{NH}_3}$, is about 200. At an absorbance ratio as high as 200, it is impossible to measure the concentration of NH_3 by an ordinary optical absorption method.

The absorption spectrum of NH_3 is a periodic spectrum with a period of 4 nm,

while that of SO_2 is a periodic spectrum with a period of 2 nm. The wavelength modulation width $\Delta\lambda$ is 3.2 nm, and the NH_3 absorption spectrum of 4-nm period provides intensity-modulated signal of angular frequency 2ω at high efficiency. The intensity-modulated signal which comes from the SO_2 absorption spectrum has a higher frequency of 3ω to 4ω . Thus, the interference from SO_2 can be lowered by using a band pass filter of 2ω in the circuit for electric signal processing.

In addition, the slit width of the spectrometer is adjusted to 2 nm for spectrum measurement as shown in Figure 4. The employment of this slit width lowers the periodicity of SO_2 absorption spectrum of period 2 nm⁽³⁾, and further reduces the interference from SO_2 .

It is not still possible to eliminate the interference from SO_2 with these measures. The analyzer therefore employs a method where the SO_2 concentration is measured simultaneously and the interference from SO_2 is removed by operational processing.

2.3 Optical System

Figure 5 shows the optical system of the analyzer. A deuterium lamp which has a flat spectrum in the ultraviolet region is used as the light source. The light emitted by the lamp passes the cell, and then enters the spectrometer. The light which entered the spectrometer is dispersed into a spectrum by the diffraction grating, and the light around the ammonia measurement wavelength (λ_0 : 209 nm) focuses on exit slit S_2 . Thus, the wavelength of exiting light is wavelength-modulated by vibrating the exit slit in the direction parallel to the direction of wavelength dispersion. The intensity-modulated signal is obtained by detecting the exiting light with photomultiplier PMT_1 .

The light around the SO_2 measurement wavelength (λ_0 : 300 nm), on the other hand, focuses on exit slit S_3 , and the intensity-modulated signal generated by absorption due to SO_2 is detected by photomultiplier PMT_2 as in the case of ammonia.

The wavelength modulation is now is now carried out by an oscillating mirror which swings the light beam in the spectrometer. Without requiring to oscillate exit slits S_2 and S_3 , this method allows to make the spectrometer more compact. In addition, the oscillation amplitude of the oscillating mirror is detected optically for its control, and the width of wavelength modulation is more consistent.

2.4 Electric Signal Processing System

The electric signal processing system is shown in Figures 7 and 8. The amplitude of AC component, A , of the intensity-modulated signal, $P_1(t)$, is detected by the lock-in amplifier (synchronous detecting circuit) and the DC component, P_0 , is obtained as the output signal of the DC amplifier. The ratio of A/P_0 is calculated by the divider, and the output signal of the divider is proportional to the NH_3 concentration (i.e., measured value of NH_3). The measured value of NH_3 , however, is superposed with an interference from SO_2 . That is,

$$(\text{Measured value of } \text{NH}_3) = (\text{True value of } \text{NH}_3) + (\text{Interference from } \text{SO}_2) \dots (6)$$

The intensity-modulated signal, $P_2(t)$, obtained at the photomultiplier, PMT_2 , for SO_2 measurement is processed by the SO_2 signal processing circuit, a circuit exactly equivalent to that for NH_3 , and the output signal of this circuit is the measured value of SO_2 .

The interference curve of SO_2 is known, and the interference from SO_2 is

determined from the interference curve and the measured value of SO_2 . The true value of NH_3 is obtained as a difference between the measured value of NH_3 and the interference from SO_2 .

2.5 Interference Curve of SO_2

Interference curves of SO_2 are shown in Figure 9. As seen in the figure, interference curves of SO_2 are not linear. In addition, they are sensitive to the NH_3 measurement wavelength and the wavelength modulation width. The interference curve changes when the measurement wavelength (209 nm) changes by +0.1 nm, and it changes also when the wavelength modulation width changes. Figure 9 shows interference curves plotted using the measurement wavelength (or wavelength modulation width) as a parameter.

Interference curves of SO_2 are stored in memory (ROM), and the value of interference from SO_2 corresponding to a measured value of SO_2 is read by a microcomputer. The interference curve to be used at the start-up of the analyzer may fall sometimes between two interference curves shown in Figure 9. To cope with such cases, an interference curve which falls between two interference curves is determined by the method of linear interpolation. Such linear interpolations are also carried out by the microcomputer.

A standard SO_2 gas of known concentration is introduced to the cell at an SO_2 span calibration. The measured value of NH_3 obtained on such standard gas corresponds to the interference from SO_2 . A new interference curve is determined from the concentration of the SO_2 standard gas and the interference from SO_2 . The SO_2 span calibration is automatically carried out at a frequency of once a week, and the new interference curve obtained through the calibration is stored in the microcomputer.

3. Measures against Thermal Drifts

The optical axis of the optical system moves due to thermal expansion and contraction of the optical system, and it causes a shift in the measurement wavelength. Such shift in the measurement wavelength leads to zero drift, span drift and drift in interference from SO_2 .

In order to minimize the move of the optical axis, the optical system is housed in a constant temperature chamber of double construction as shown in Figure 10. Figure 10(a) shows the optical system itself without its casing. All optical system components other than the cell, which is heated to high temperature, are housed in the constant temperature chamber (see Figure 10(b)).

The constant temperature chamber is maintained at 43°C. The temperature is controlled by the heater installed in the inner casing and the cooling air introduced between the inner and outer casings. The cooling between the inner and outer casings is necessary because the optical system has many heat-emitting components such as the lamp, heated cell and heated sampling channel.

4. Basic Configuration

The whole sample path from the sample inlet to the cell outlet is heated by a heater as shown in Figure 11. The heating temperature is 300°C except the dust filter (filled with glass wool) which is heated to 400°C.

Calibrations, selection of SO_2 interference curve and back-blowing are carried out automatically by a microcomputer installed in the system.

The back-blowing system is essential because ammonia molecules are easily adsorbed to dust. The high pressure gas for back-blowing is heated to 300°C at the preheating tube before it enters the sample path in order to prevent deposition of acid ammonium sulfate that would otherwise deposit when the sample path is cooled at back-washing.

5. Sampling System

5.1 Sampling Temperature(5)

Sulfuric anhydride (SO_3) contained in the flue gas would react with ammonia into acid ammonium sulfate in the process of gas sampling. Such reactions are detrimental to the measurement of ammonia. It is known that the disposition temperature of acid ammonium sulfate depends on the ammonia and SO_3 concentrations, and that it is on the order of 235°C when ammonia and SO_3 concentrations are on the order of 5 ppm and 10 ppm, respectively. Measurements on actual flue gas, however, revealed that disposition of acid ammonium sulfate occurs below 250°C. It is therefore necessary to carry out gas sampling at temperatures exceeding 250°C.

Ammonia molecules, on the other hand, are adsorbed easily to dust in flue gas and walls of the sample path. An extreme adsorption of NH_3 deteriorates the responsiveness of the analyzer, and examinations from this viewpoint are also necessary.

When the temperature of sample path is higher, adsorbed molecules have more thermal energy and are desorbed more easily. Thus, the level of adsorption becomes lower in appearance at high temperatures. Table 1 shows a relation between the response times and the sampling tube temperature obtained by measuring leak ammonia through a sampling tube (nickel) of 16 m long. Table 1 shows that the analyzer response is fast when the sampling temperature is 330°C or higher indicating a low level of adsorption at such temperatures.

5.2 Gas-Contacting Materials(5)

At measuring the flue gas containing SO_3 , a care must be paid to the gas-contacting materials used in the sample path. Such materials as stainless steel SUS316, titanium and zirconia behave as catalysts for deposition of acid ammonium sulfate. If such metals are used in the sample path, some ammonia is lost to the chemical reaction, and the measurement of ammonia cannot be performed correctly. The optimum gas-contacting material for the sample path is stainless steel SUS304, which causes no chemical loss of ammonia. Nickel does not cause chemical loss of ammonia either, but it is susceptible to corrosion in a long use.

5.3 Dust Removal(5)

A dust filter filled with glass wool is included in the ammonia analyzer. Not to deteriorate the responsiveness, the glass wool temperature must be maintained at a temperature (400°C) higher than the sampling tube temperature. When much dust accumulates on glass wool, the response slows down even when the temperature is maintained at 400°C. A mesh filter (5 μm) is attached at the tip of the probe to reduce accumulation of dust on glass wool so that glass wool can be changed less frequently.

The mesh filter at the tip of the probe is get clogged, and back-blowing is necessary. The back-blowing is performed at a frequency of once every six hours for the dust concentration of 15 g/ Nm^3 , but one back-blowing in a month is adequate for low dust systems. As described earlier, the back-blowing is carried out automatically by the built-in back-blowing system.

The glass wool is replaced once every week or every two weeks, but once in one to three months is adequate for low dust systems.

5.4 Sampling System⁽⁵⁾

The structure of the sampling system is shown in Figure 12. Some features of this structure include that all system from the probe to the cell is heated to temperatures higher than 330°C, that the gas-contacting material at heated parts is SUS304 and that it is designed to minimize the accumulation of dust in the sample path.

Details of the sampling system include the following:

- The probe portion which is coming into the duct from the flange is also heated by a heater.
- All connections including those between the probe and the sampling tube, between sampling tubes and between the sampling tube and the sample inlet of the analyzer are heated by heaters.
- A mesh filter is attached to the tip of the probe to minimize dust which enters the sampling tube.
- A glass wool filter heated to 400°C is used in the analyzer to remove dust.
- The system carries out back-blowing automatically with heated air of 300°C or higher.

6. Correlation with Manual Analysis⁽⁵⁾

Figure 13 shows the correlation between values obtained by the ammonia analyzer and those obtained by manual analysis. The figure indicates that the values obtained by the ammonia analyzer agree well with those obtained by manual analysis. The correlation coefficient is 0.92, and the deviation from the line with a slope of 45° is 0.8 ppm at maximum.

The deviation includes not only errors of the analyzer but also those of manual analysis. Thus, the errors of the analyzer can be much smaller. The manual analysis was carried out using the indophenol method (JIS K 0099). Figure 14 shows an example of analyzer recording obtained while manual analysis was also going on.

7. Major Specifications and Stability

The ammonia analyzer has two measurement ranges of 0 to 20 ppm and 0 to 50 ppm. The measurement range for SO₂ is 0 to 2,000 ppm. The 90% response time is 2 minutes maximum.

The automatic zero-point calibration is carried out every six hours, and the automatic span calibration is carried out once a week. With these calibrations, the zero-point drift is within ± 0.4 ppm ($\pm 2\%$ FS) for NH₃ and the span drift is within $\pm 2\%$ FS for both NH₃ and SO₂. The zero-point drift for SO₂ is within $\pm 0.5\%$.

As described earlier, the analyzer removes the interference from SO₂ through the simultaneous measurement of SO₂ concentration. Therefore, the measurement error which comes from drift in SO₂ indication and the error involved with correction for interference (which mainly comes from the drift of the interference curve) are superposed in the indication error of NH₃. Taking these errors into consideration, the total error at measuring NH₃ of 5 ppm is ± 0.8 ppm at maximum.

8. Comparison with Indirect Ammonia Analyzer

The ultraviolet ammonia analyzer is a direct ammonia analyzer which measures ammonia directly without any chemical conversion. The reduction catalyst type ($\text{NH}_3\text{-NO}$ denitrification reaction type) ammonia analyzer is an indirect ammonia analyzer which measures reduction of NO_x on the ground that the reduction of NO_x in the denitrification reaction is equivalent to ammonia concentration.

Table 2 compares the direct and indirect ammonia analyzers, and a detailed discussion is given below.

8.1 Principle and Features of Reduction Catalyst Type Ammonia Analyzer

It is necessary to know some measurement principles of the indirect ammonia analyzer before direct and indirect ammonia analyzers are compared. Thus, the principle of indirect ammonia analyzer is explained first.

Figure 15 shows a basic configuration of indirect ammonia analyzer. It has two sampling channels, and a catalyst for $\text{NH}_3\text{-NO}$ denitrification reaction is provided at the tip of one sampling channel. The NO_x concentration of the sample introduced to the NO_x analyzer through this channel lower than that of the flue gas by the amount of the NH_3 concentration consumed in the denitrification reaction.

The NO_x concentration of the sample introduced to the NO_x analyzer through the other sampling channel is equivalent to that of flue gas.

The NH_3 concentration is obtained as a difference in NO_x concentrations measured by the NO_x analyzer while switching between the two sampling channels. The NO_x analyzer used for this purpose mainly employs the chemical luminescence method because of its high sensitivity.

As understood from the principle stated above, the advantage of the indirect ammonia analyzer is that it allows to obtain concentrations of NH_3 and NO_x at a time.

Disadvantages of the indirect ammonia analyzer include the following:

- The indirect ammonia analyzer can not be calibrated as an ammonia analyzer.
- A small air leakage in either channel (negative pressure) causes a large error in the measured value of NH_3 . An air leakage of 1% in measuring a flue gas of 200 ppm NO_x , for example, results in an error of 2 ppm NH_3 .
- The catalyst activity deteriorates as time passes, and it causes a NH_3 concentration lower than actual concentration (i.e., the negative error increases). In addition, there is no means for checking the deterioration of catalyst activity.
- The switching of two channels from one to the other causes a large error in transient state where the variation in NO_x concentration is large.

8.2 Features of Direct (Ultraviolet) ammonia Analyzer

The foremost advantage of the ultraviolet ammonia analyzer is that it provides measured values of high reliability.

Disadvantages of the ultraviolet ammonia analyzer include the following:

- Power consumption is large because of high temperature gas sampling for the analyzer.
- The analyzer is large in size, and requires a large space for its installation.
- The analyzer is costly.

9. Use of Ultraviolet Ammonia Analyzers

Ultraviolet ammonia analyzers actually in use as leak ammonia monitors are listed in Table 3. These analyzers are operating in good condition without any major troubles.

Ammonia analyzers with such functions as automatic SO₂ interference compensation and automatic zero-point and span calibration are used as leak ammonia monitors for flue gas denitrification of coal fired power plants. Ammonia analyzers for other applications do not have the function of automatic SO₂ interference compensation. Ammonia analyzers without automatic calibration and automatic back-blowing functions are used for applications other than utilities.

10. Summary

Ammonia analyzers used as leak ammonia monitors used mainly with flue gas denitrification equipment of coal fired power plants were described with an emphasis on the ultraviolet ammonia analyzer.

Direct and indirect ammonia analyzers have their own advantages and disadvantages, but it can be said that the direct ammonia analyzer is more favorable from the viewpoint of catalyst management of denitrification equipment, where a priority should be given to the reliability of measured NH₃ concentrations.

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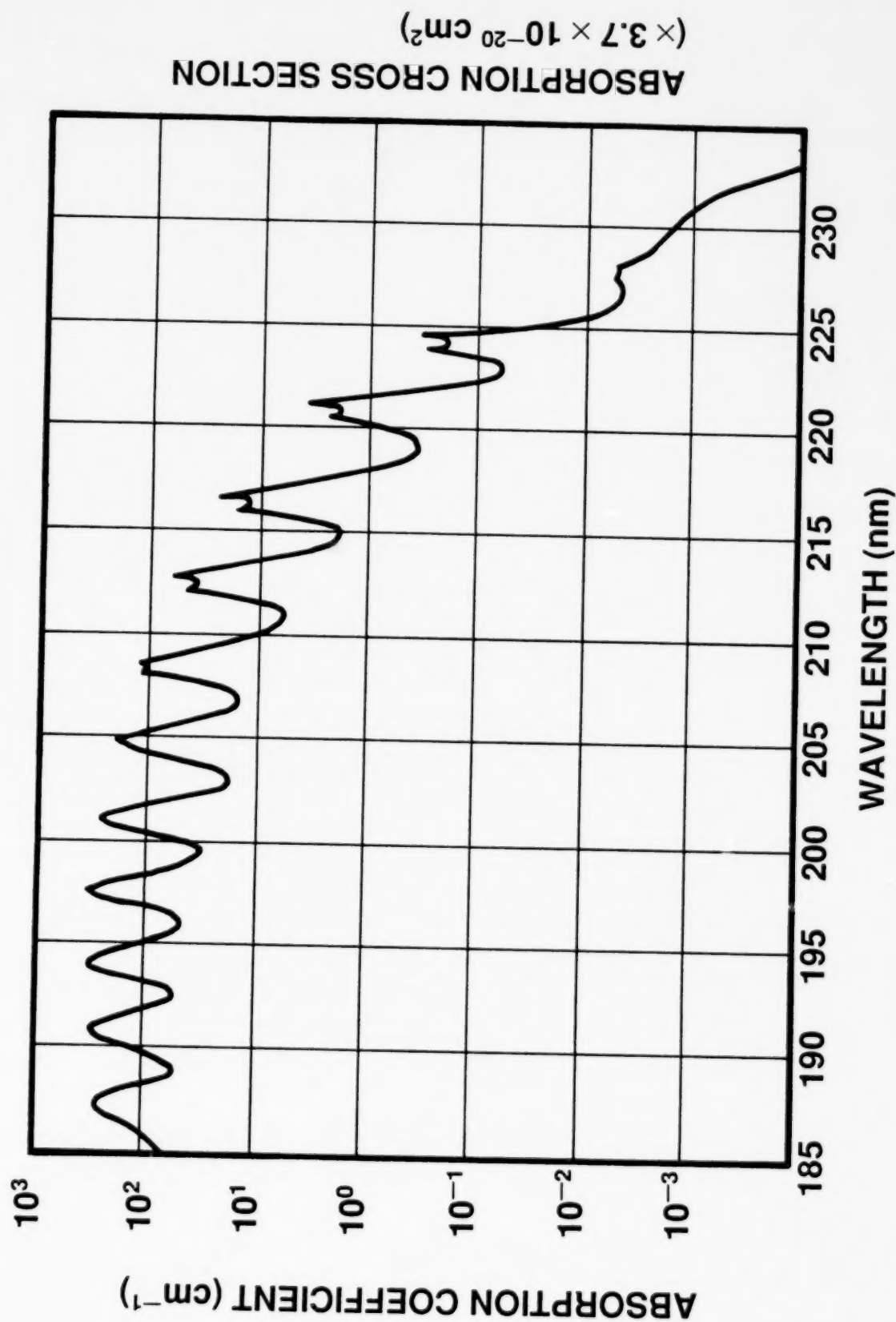


Figure 1. Ultraviolet absorption spectrum of ammonia

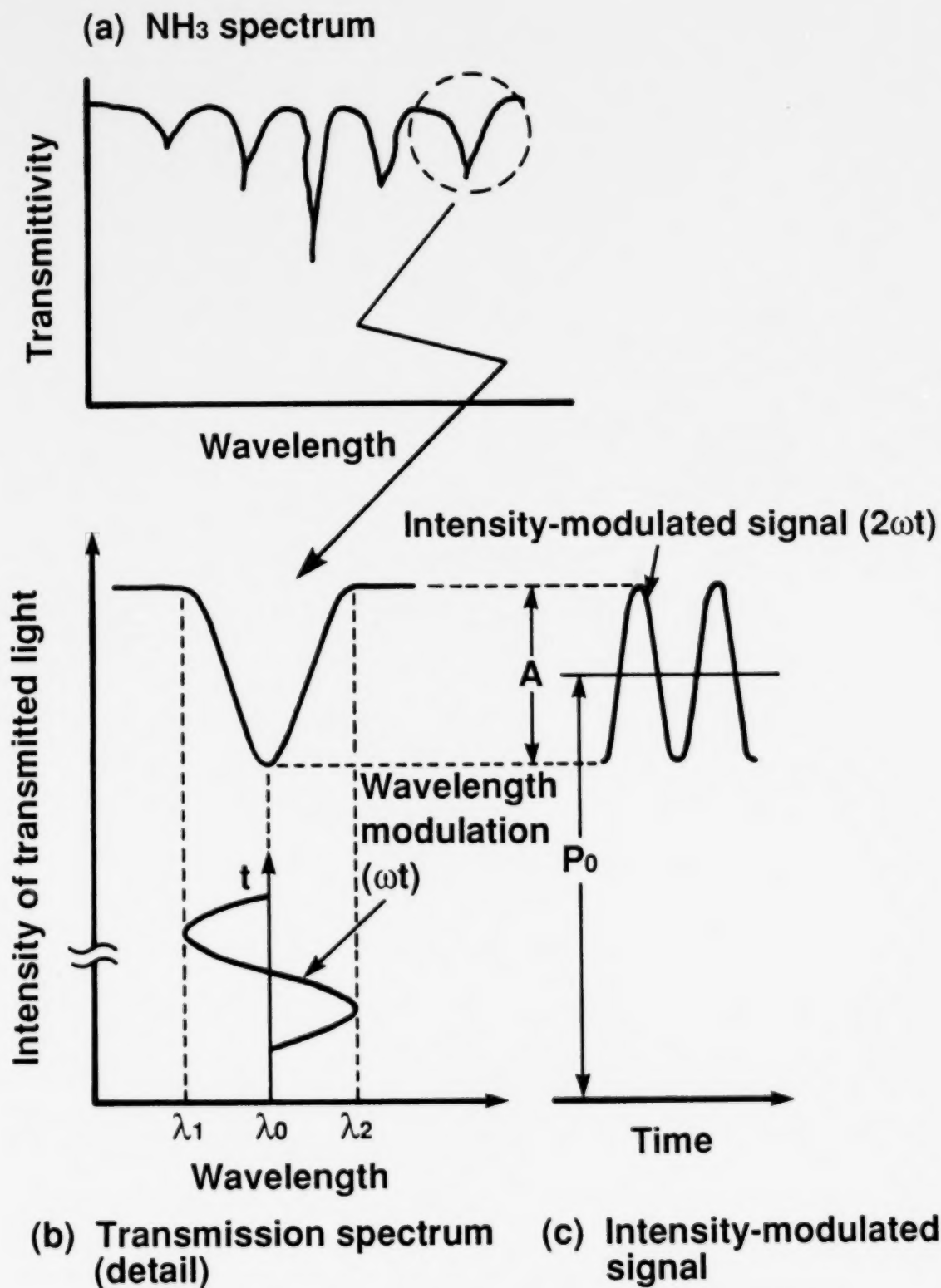


Figure 2. Explanation of principle

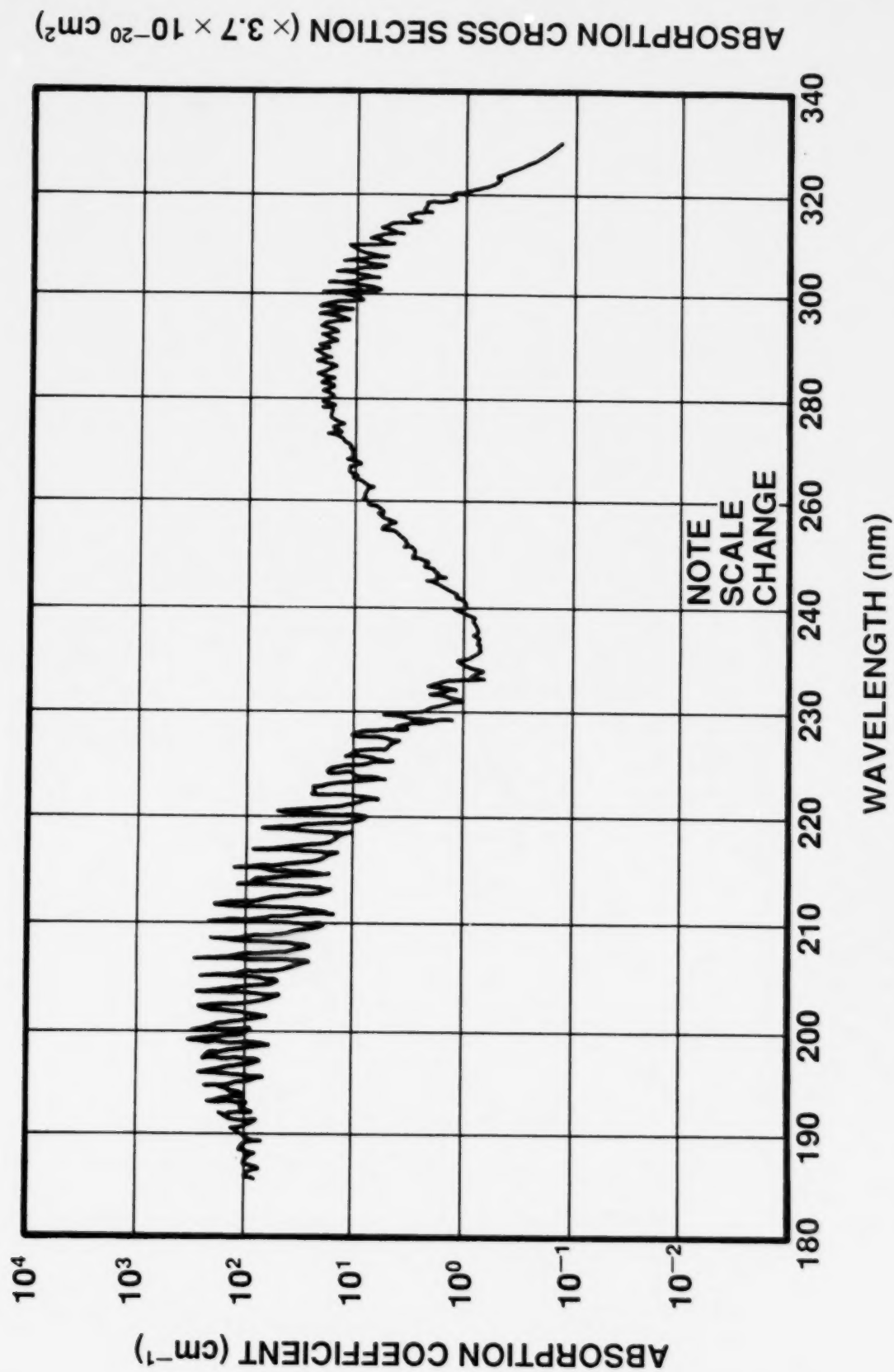


Figure 3. Ultraviolet absorption spectrum of SO_2

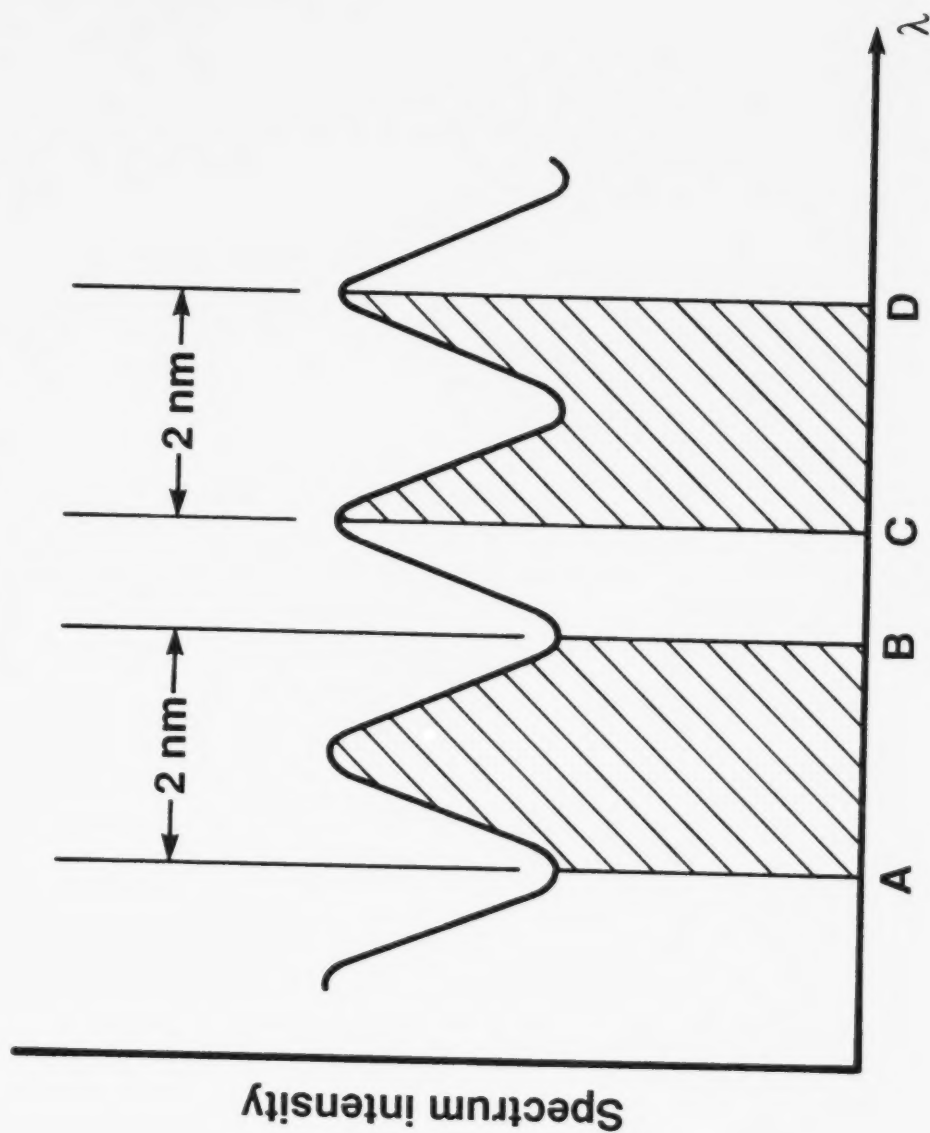


Figure 4. Relation between synchronous spectrum of SO_2 and slit width of spectrometer

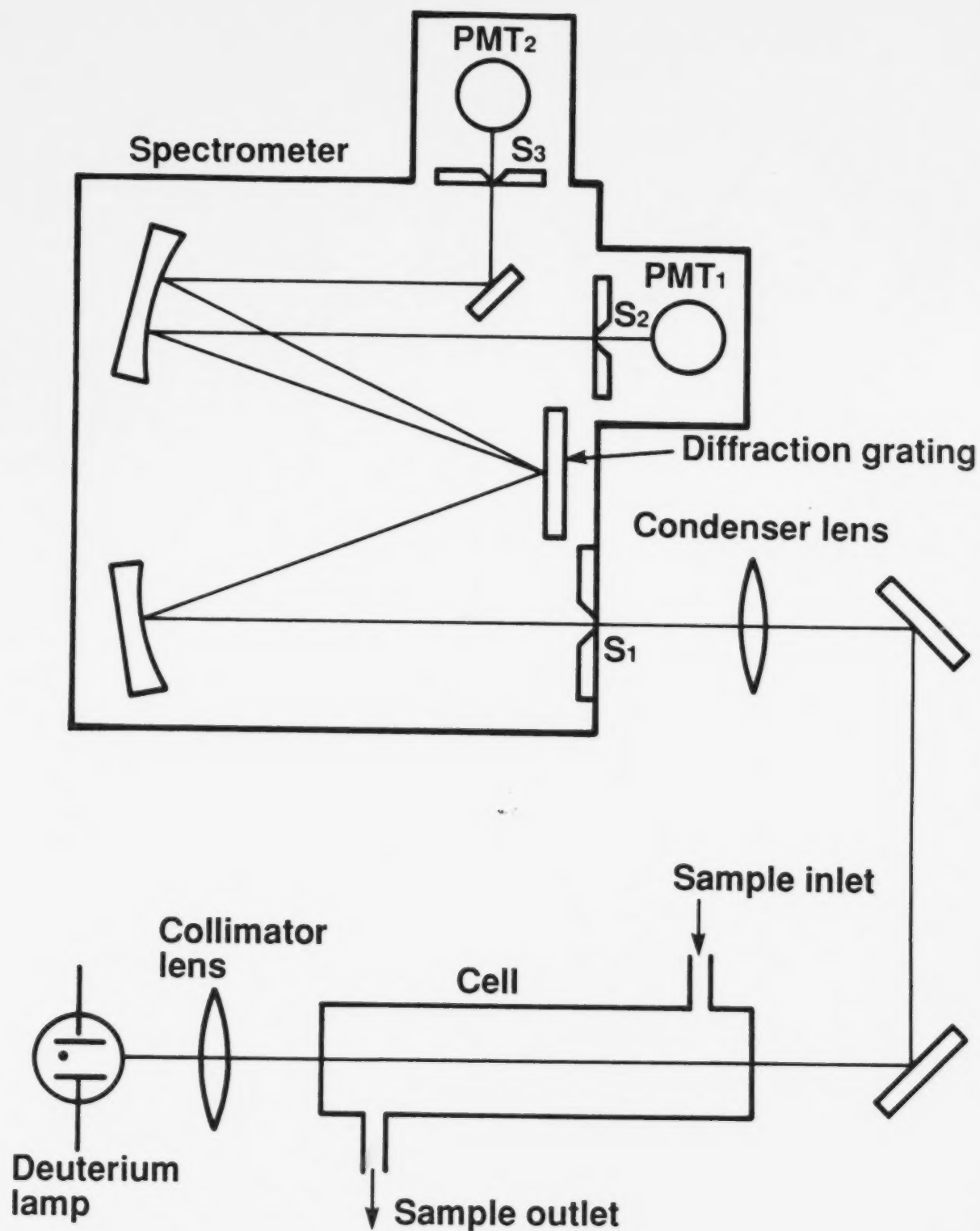


Figure 5. Optical system

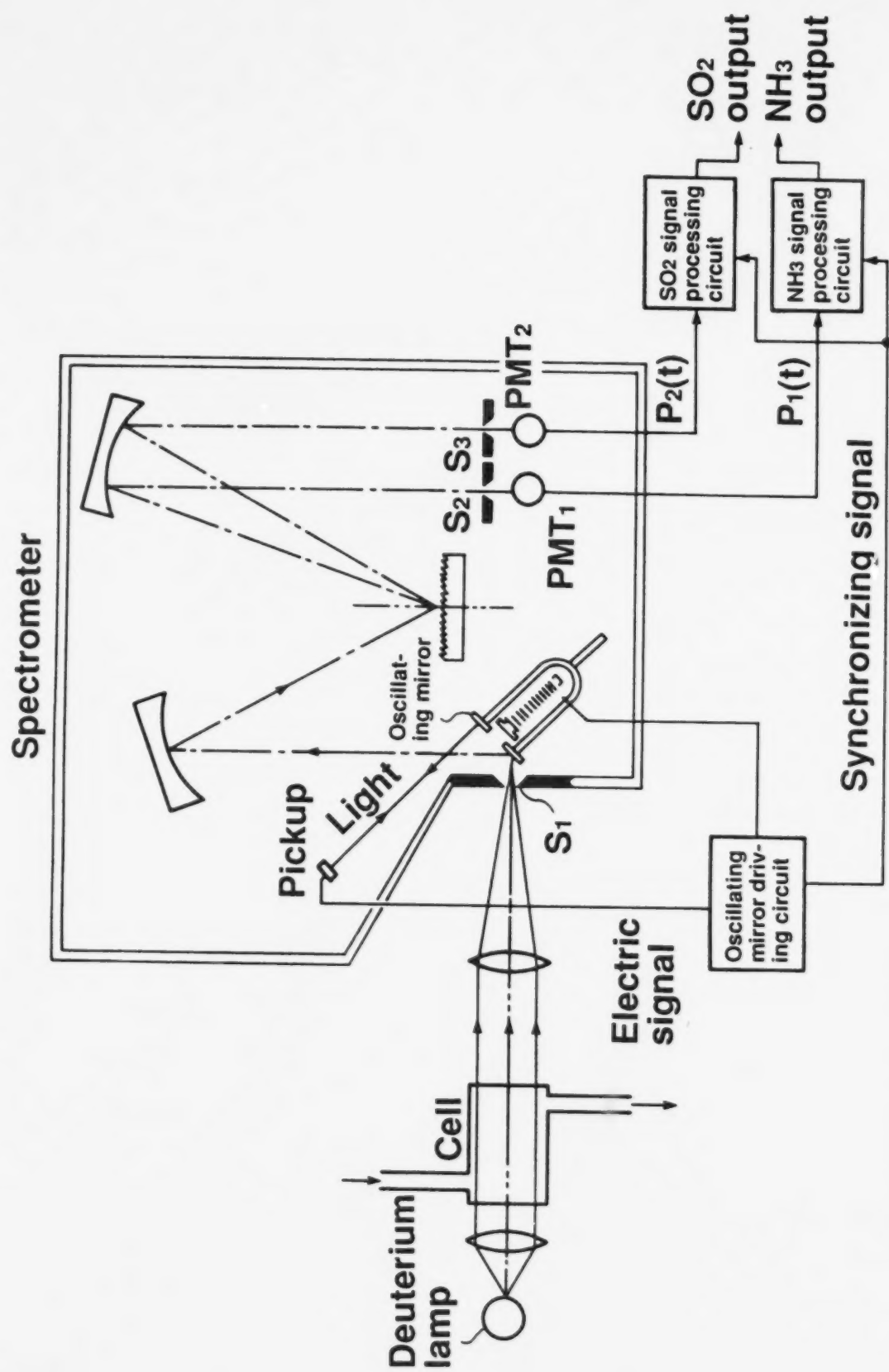


Figure 6. Basic configuration of detection system

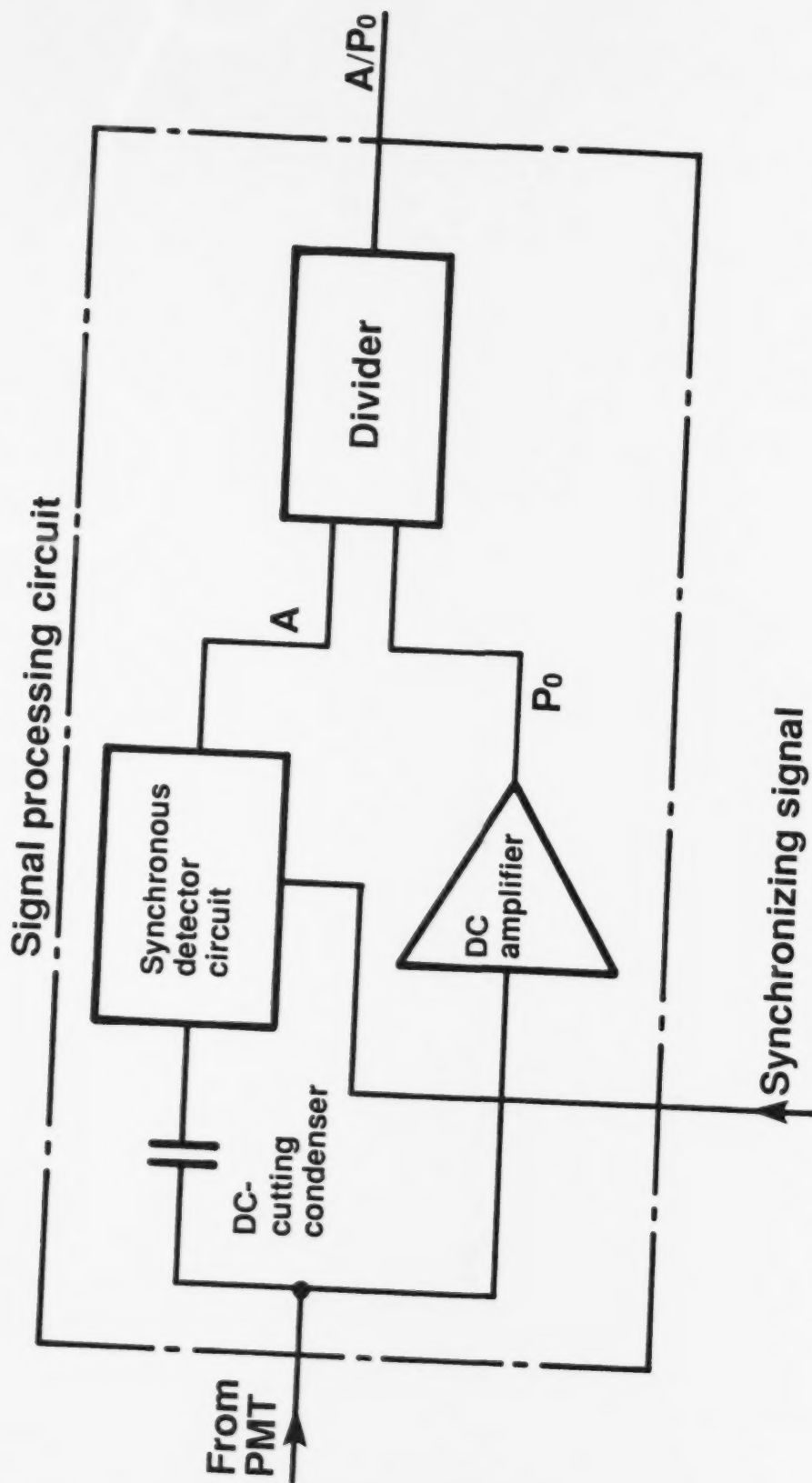


Figure 7. Block diagram of signal processing circuit

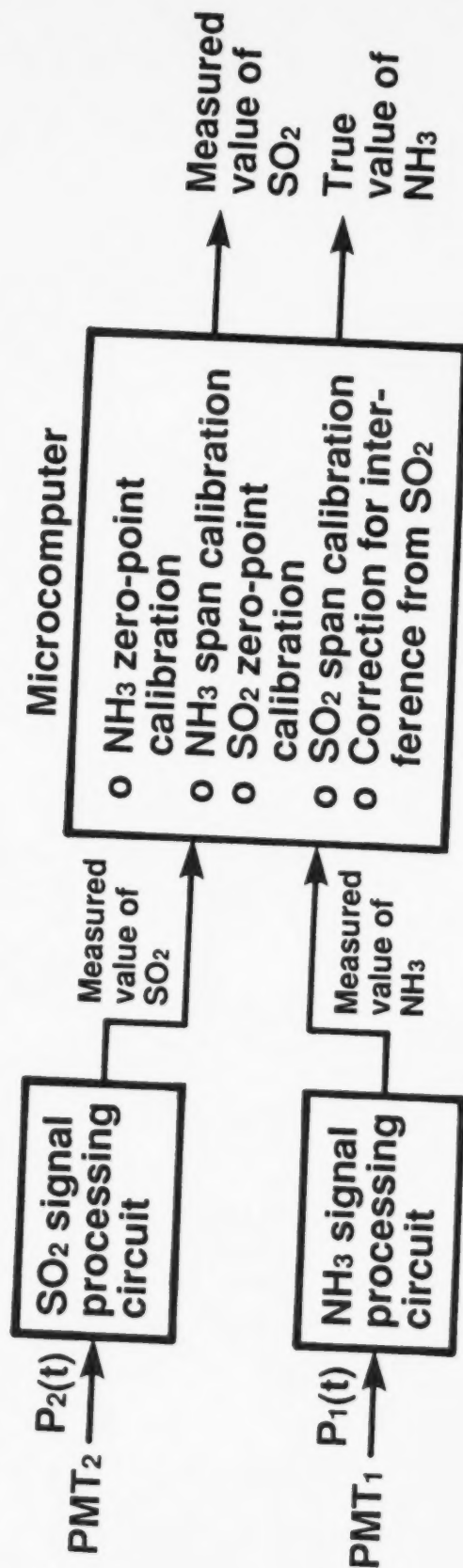


Figure 8. Electric signal processing system

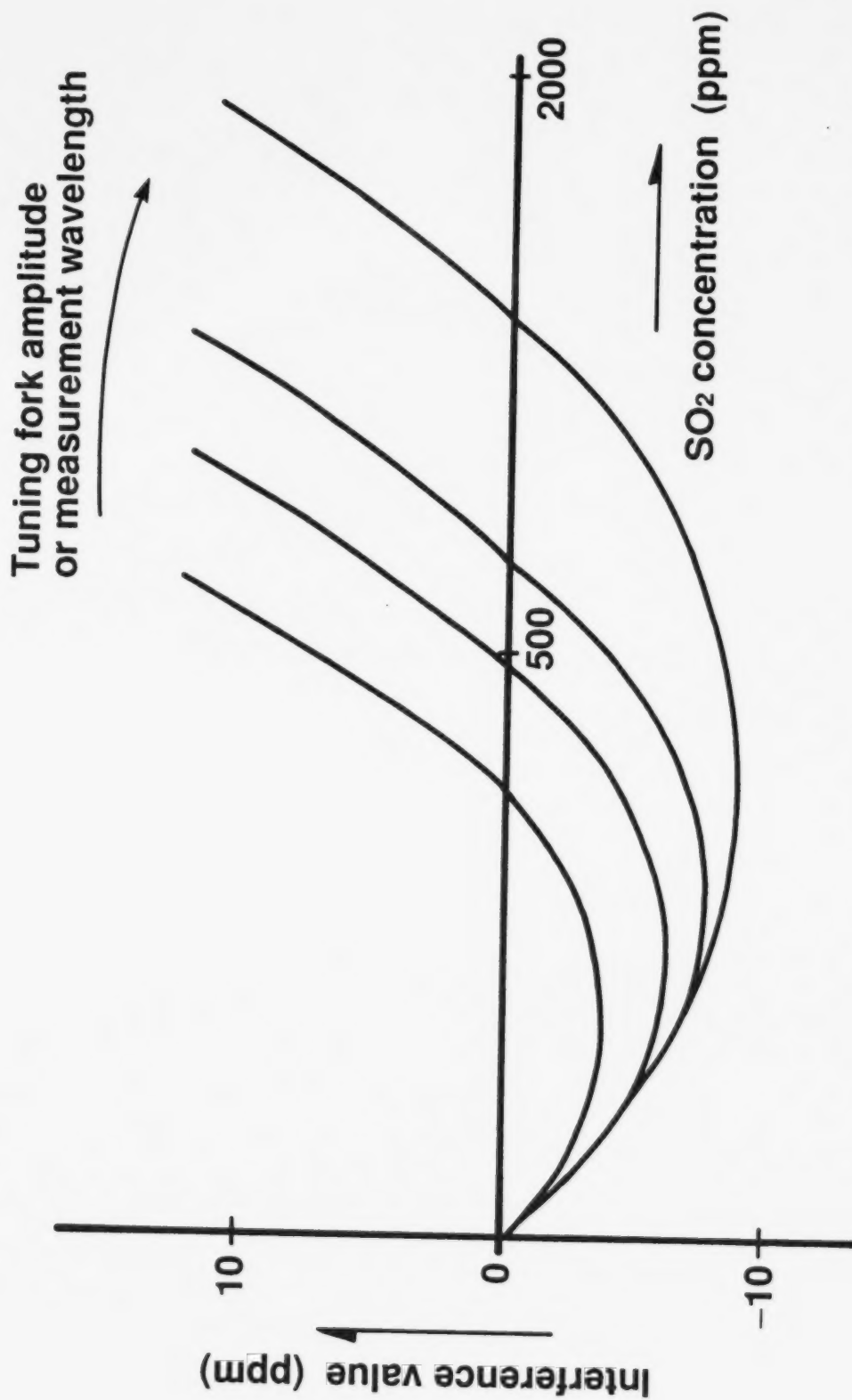


Figure 9. Interference curves of SO₂

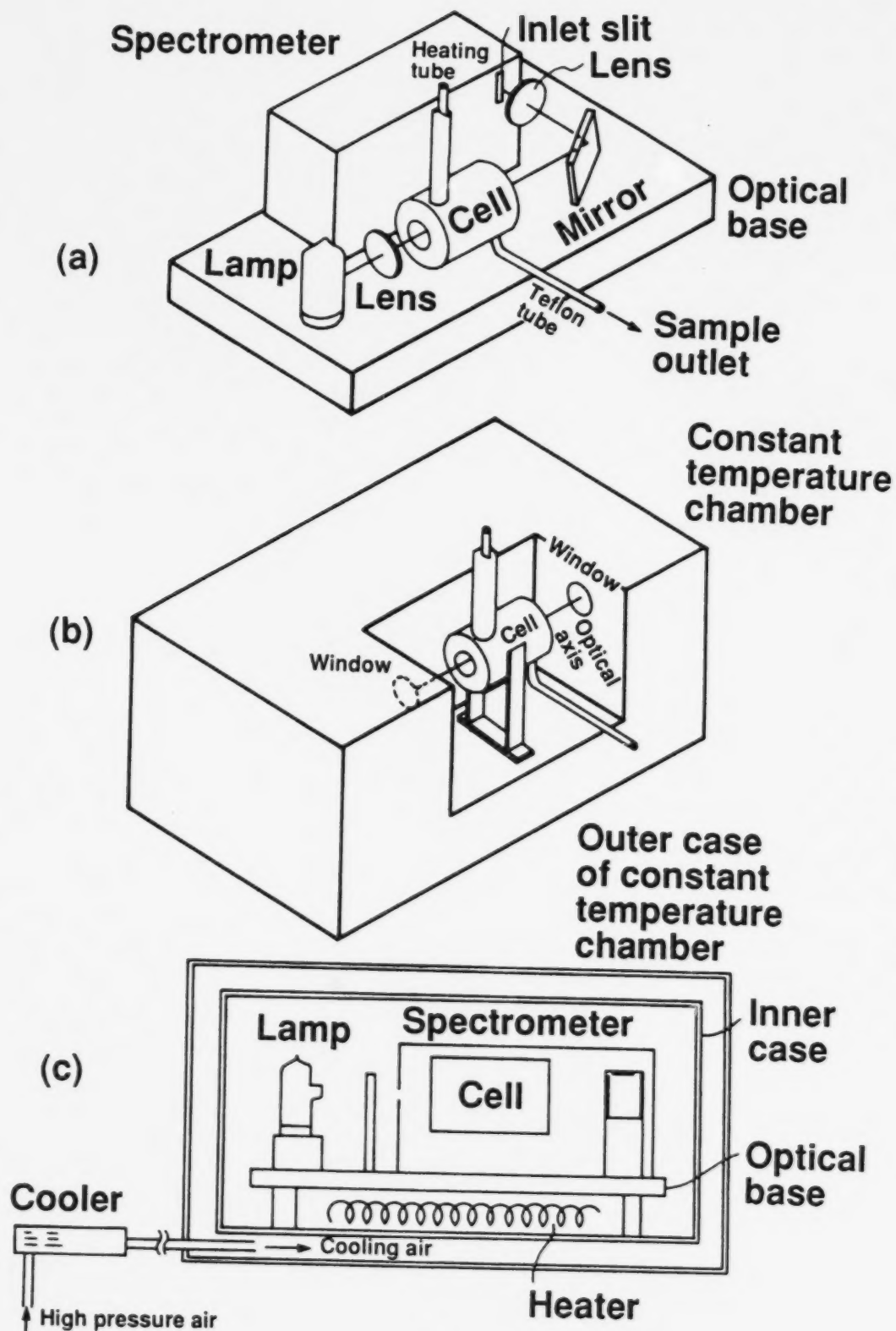


Figure 10. Construction of optical system

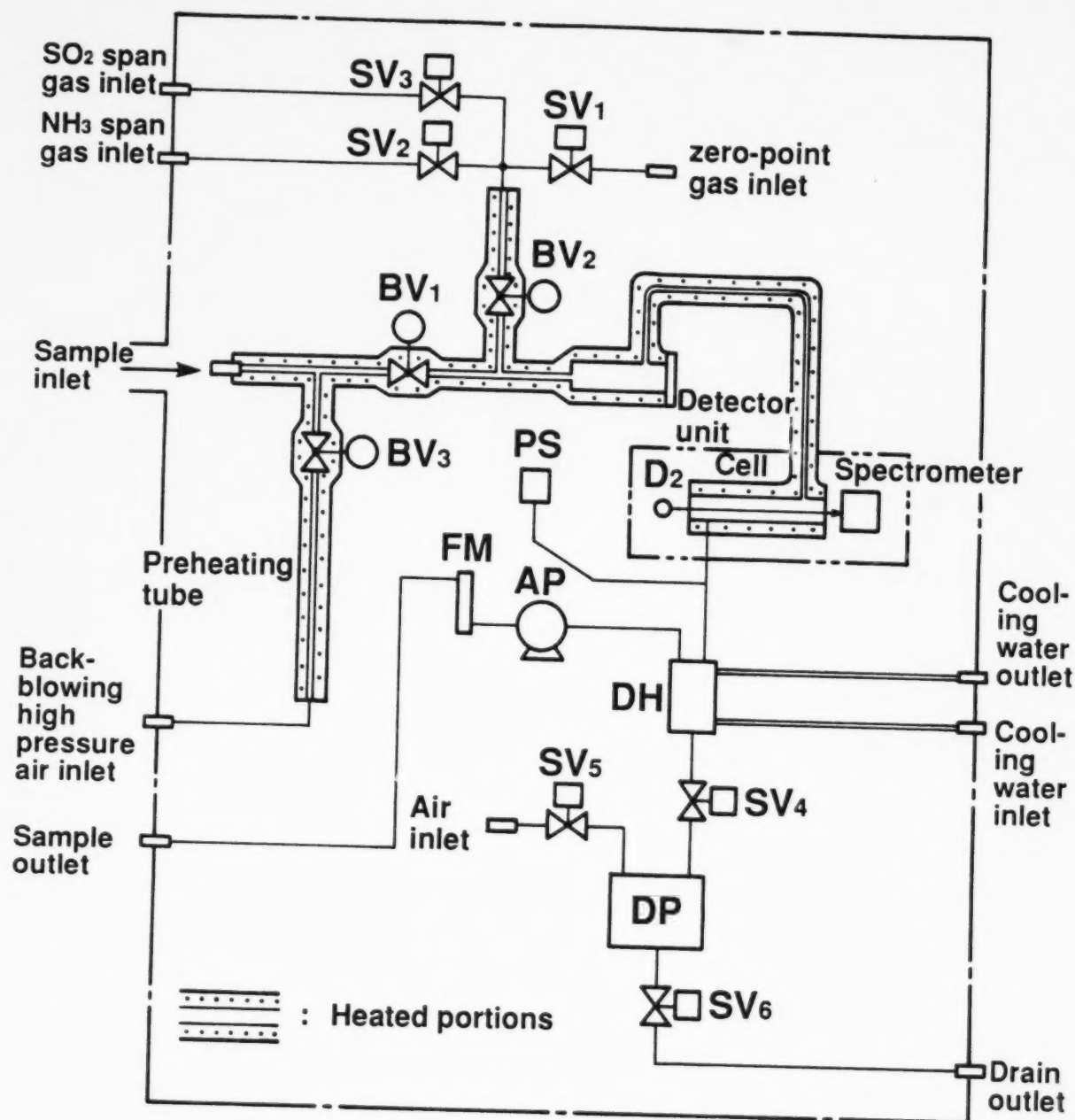


Figure 11. Basic configuration of NH_3 analyzer

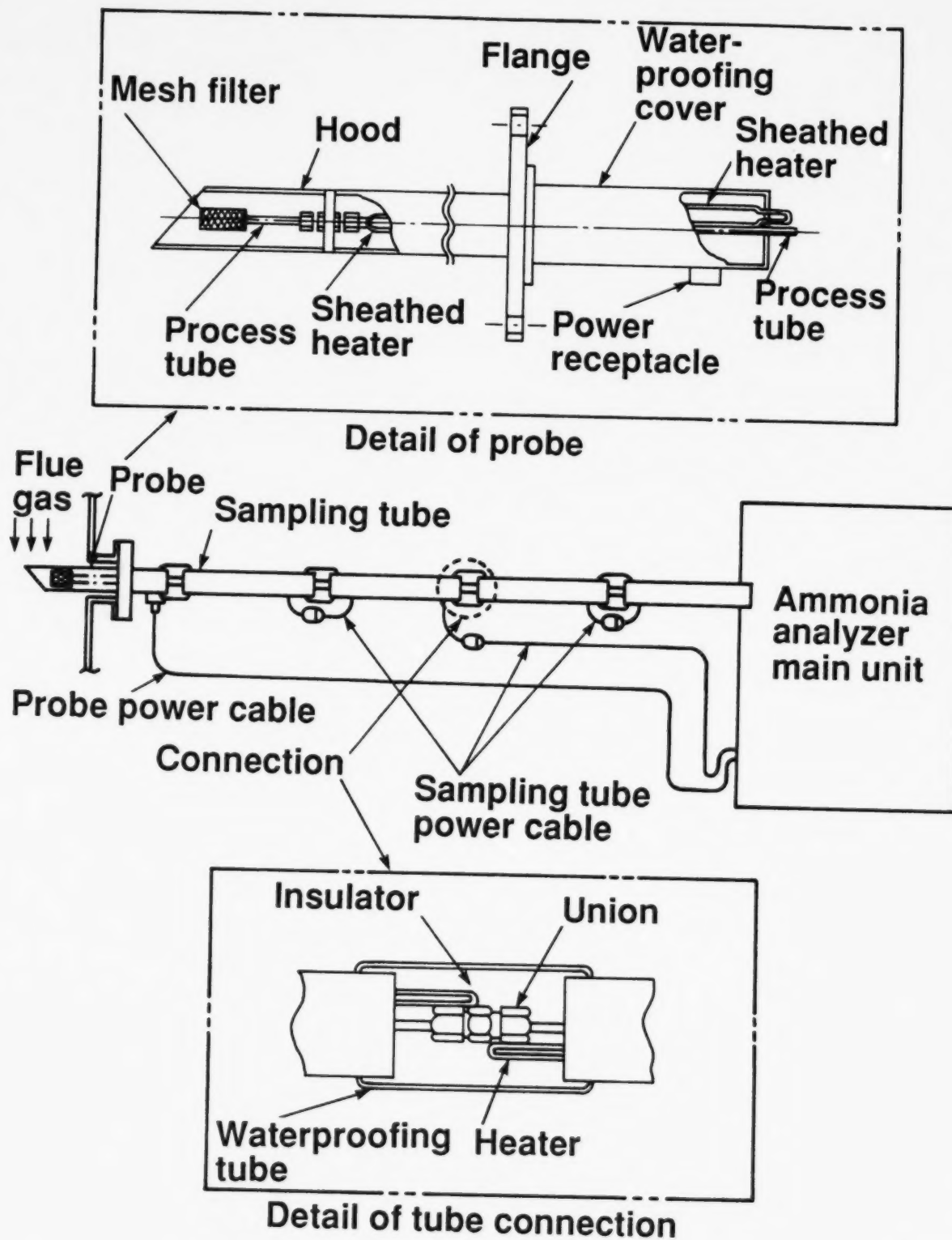


Figure 12. Structure of sampling system

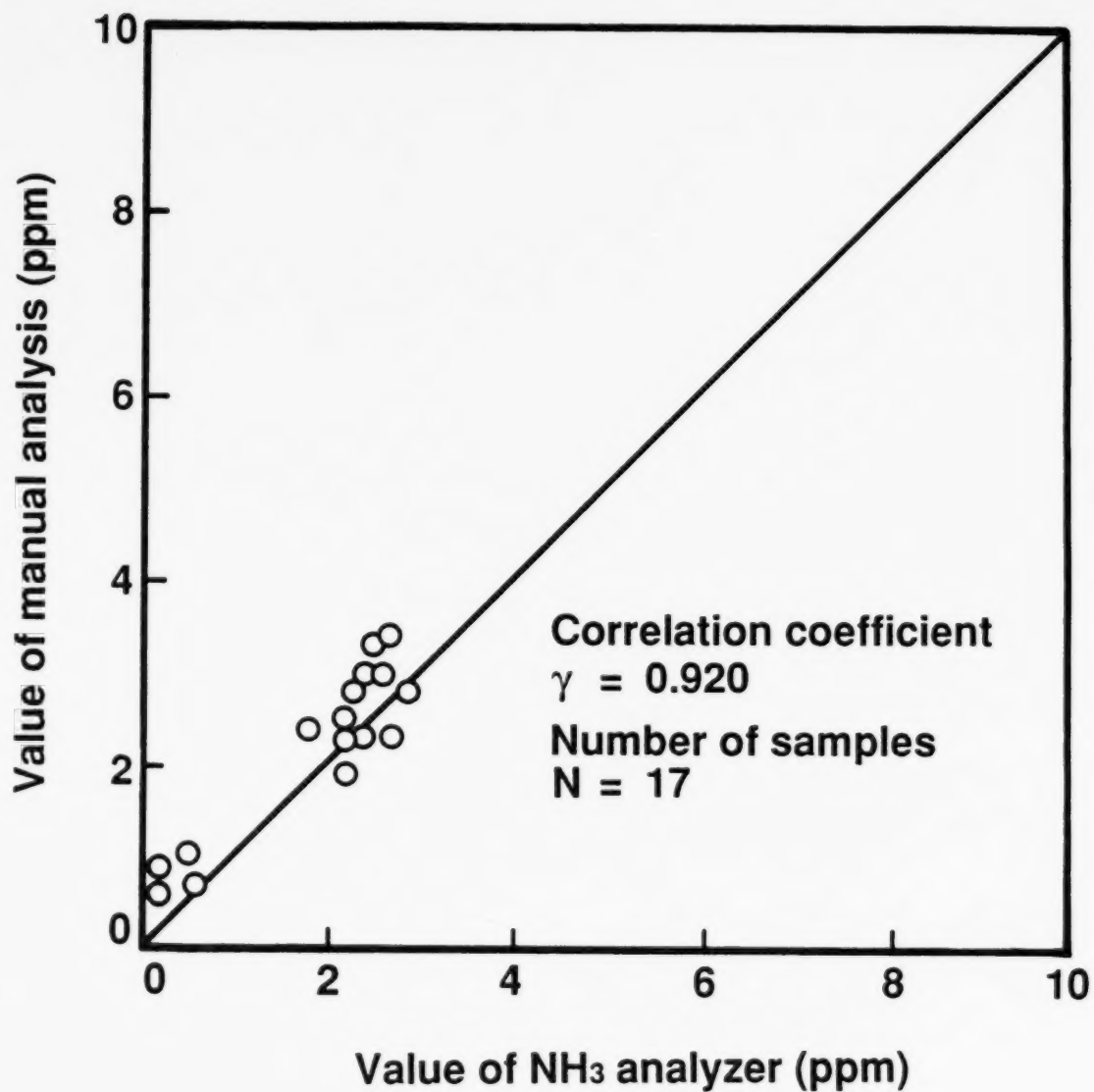


Figure 13. Correlation between values of analyzer and manual analysis

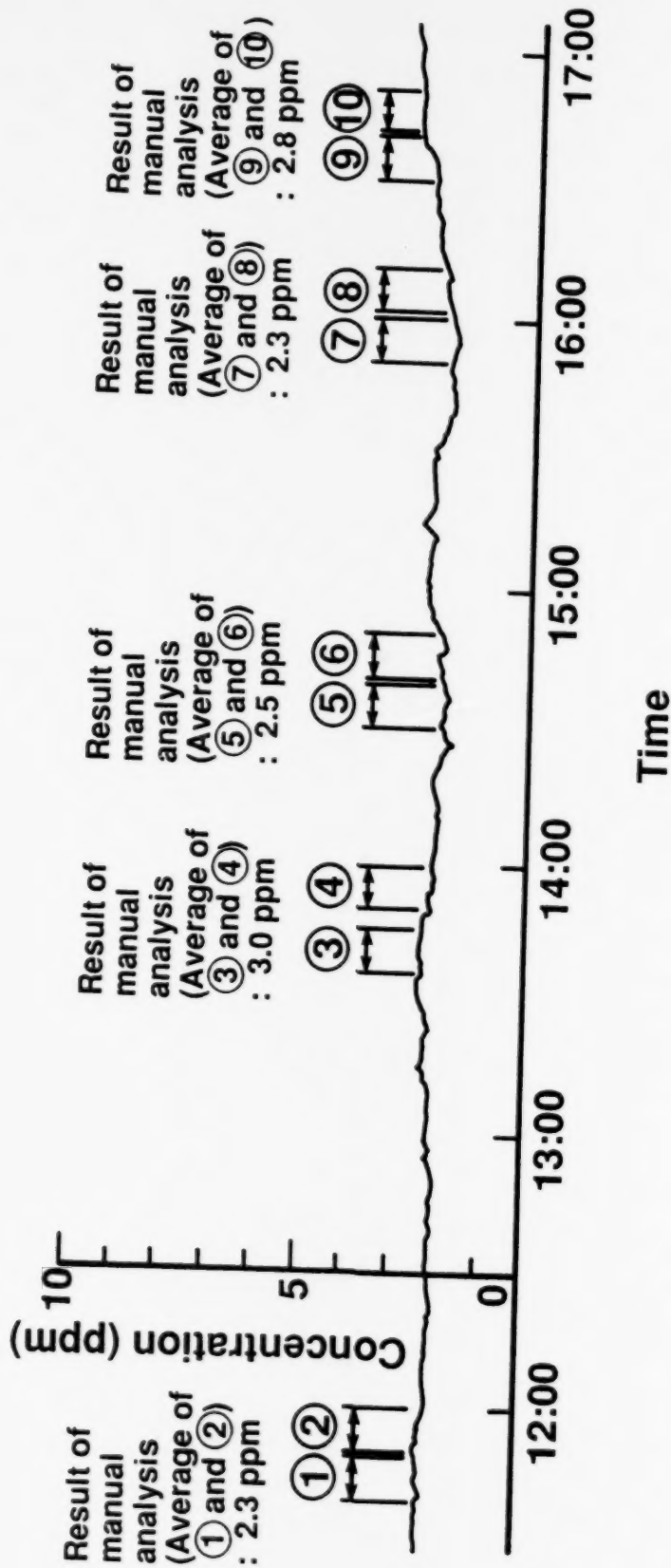


Figure 14. Example of analyzer recording

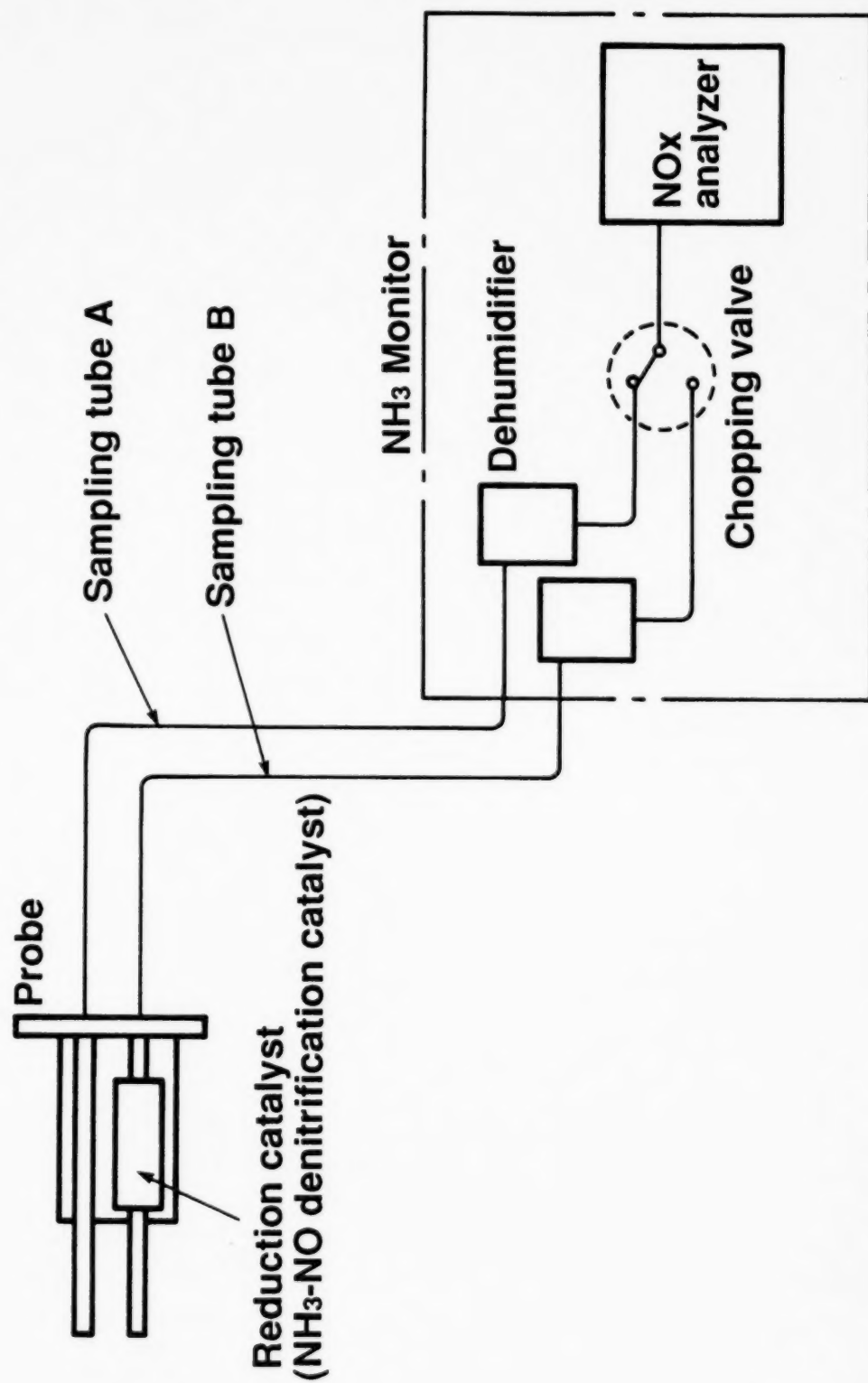


Figure 15. Basic configuration of indirect ammonia analyzer

**TABLE 1. RELATION BETWEEN SAMPLING
TUBE TEMPERATURE AND
RESPONSIVENESS**

Sampling tube temperature	90% response time	
	Rising edge	Falling edge
250°C	3 min 17 sec	6 Over 6 min
300°C	3 min 10 sec	3 min 6 sec
330°C	2 min 50 sec	2 min 50 sec
350°C	2 min 45 sec	2 min 48 sec
400°C	2 min 40 sec	2 min 30 sec

TABLE 2. COMPARISON OF DIRECT AND INDIRECT ANALYZERS

	Indirect analyzer	Direct analyzer
Advantages	• NH_3 and NO_x are measured simultaneously.	• Measurement reliability is high.
Disadvantages	• Calibration of analyzer as NH_3 analyzer is not possible. • Small air leakage in the sampling channel causes a large measurement error. • There is no way of checking the deterioration of catalyst activity. • When NO_x concentrations varies much, measurement error becomes large for transient state.	• Power consumption is large. • The analyzer is large in size. • The analyzer is costly.

TABLE 3. USE OF AMMONIA ANALYZERS

Type of facility		Place of installation	Start of operation	Number of units	Type of NH ₃ analyzers
Coal fired power plant denitrification	Low dust system	Takehara #3, EPDC	March 1984	2	Automatic compensation of interference from SO ₂
	High dust system	Minato Power Plant, Kyushu EPC	August 1986	1	Automatic calibration Automatic back-blowing
Oil fired power plant denitrification		Ooi Power Plant, Tokyo EPC	March 1985	1	Automatic calibration Automatic back-blowing
LNG composite cycle power plant denitrification		Futtsu Power Plant, Tokyo EPC	September 1987	7	
			Planned to start in September 1987	7	
Others • Steel sintering furnace flue gas denitrification • Refuse incinerator flue gas denitrification • Sludge incinerator flue gas denitrification • Flue gas denitrification in nitric acid production process • Others			March 1980	1	Manual calibration
			January 1987	1	
			March 1983	3	
			December 1985	2	
				3	

UPDATED TECHNICAL AND ECONOMIC
REVIEW OF SELECTIVE CATALYTIC
NO_x REDUCTION SYSTEMS

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ABSTRACT

Selective Catalytic NO_x Reduction is now being used on coal-fired units in Japan, in both retrofit and new unit applications. This update lists Japanese coal-fired units using SCR. In addition, it updates the technical design requirements to help prevent air heater plugging by ammonia-sulfur compounds. The major new requirement is a lower NH₃ slip limit of 3 ppm to 5 ppm which in turn requires significantly lower space velocities. Hence greater catalyst volumes and process costs are realized than were identified 2 or 3 years ago (See Reference 1). In addition, the impact of the devaluation of the dollar against the yen is reviewed. Current SCR cost analyses for a new utility coal-fired unit application, and retrofit utility coal-fired units are provided. The new Industrial NSPS NO_x limits are presented and an SCR cost analysis on a small industrial generator is reviewed. Finally, conclusions based on Japanese SCR experience in terms of updated costs and its present applicability to U.S. coal-fired units are presented.

INTRODUCTION

Selective Catalytic Reduction (SCR) is now being used in Japan to control NO_x emissions from natural gas, oil and coal-fired combustion. SCR has not found commercial acceptance in the United States. The principal reasons are its high costs on all fuel applications and potential technical problems with U.S. coal ash. In spite of these concerns, interest is growing because of the low NO_x emissions achievable by this technology. California has enacted guidelines (See Reference 2) for new coal-fired power generating units which limit full load emissions to 0.09 lb/MBtu which virtually mandates SCR. New Mexico and New Jersey are following this lead and are reviewing SCR as a feasible and viable means of NO_x control. New Jersey may require it as "Best Available Control Technology" (BACT). Hence, it is important for U.S. industrial and utility companies to keep abreast of SCR technical and cost considerations.

PROCESS DESCRIPTION

NO_x REDUCTION

The Selective Catalytic Reduction (SCR) process uses ammonia (NH₃), in gaseous form, which is diluted with air to about 5 percent by volume and injected into the flue gas stream. The NH₃ reacts with the NO_x, in the presence of catalyst, at reaction temperatures ranging between 600°F and 750°F for low and medium sulfur coal applications, as shown in equations (1) and (2) below. For high sulfur coals emitting 2000 ppm SO₂ or more (i.e., approximately 5.0 lb/MBtu or more), Reference 1 states that the reaction temperature range should be restricted to 650°F to 750°F to prevent catalyst poisoning.

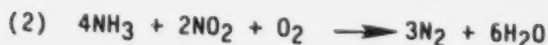
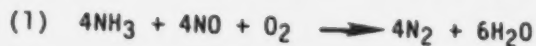
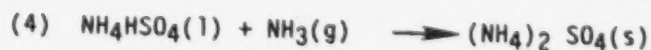
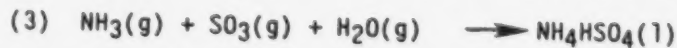


Figure 1 shows the physical placement of SCR catalytic reactor(s) in the boiler's flue gas stream. It is so placed to insure that the process temperature requirements are met. The optional economizer flue gas bypass, also shown in Figure 1, ducts hot economizer inlet flue gas directly to the economizer exit. This option is used to maintain the process reaction temperatures during low loads. In the case of mid-western and eastern U.S. high sulfur coals, this may be a necessity to provide NO_x control over a wide load range. In California, where low sulfur coals would be burned, the guidelines for new coal-fired plants (Reference 2) do not require this option and NH₃ injection can be terminated below 600°F.

NO_x at the economizer outlet typically is assumed to consist of 95% NO and 5% NO₂. Hence the theoretical stoichiometric ratio for 100 percent reduction is 1.05:1, NH₃:NO_x mole ratio (see equations (1) and (2)). The actual NH₃:NO_x ratio used is a function of NO_x reduction required, inlet NO_x concentration, and the acceptable NH₃ "slip," where "slip" is that unreacted ammonia which slips past the SCR reactor(s). It should be noted that the NO_x emitted from the boiler rapidly converts to NO₂ in the atmosphere and thus NO_x regulations state emission limits in lb/MBtu NO₂ equivalent.

AMMONIUM BISULFATE/SULFATE FORMATION

Excess ammonia in the flue gas combines with the SO₃ in the flue gas to form ammonium bisulfate and ammonium sulfate as shown in the equations below:



Current regenerative air heater designs consist of hot end, intermediate, and cold end baskets (see Figure 2 without SCR). It is important to note that there is a physical space between each of the three sections. Ammonium bisulfate tends to liquefy (i.e., at about 410°F) in the intermediate baskets. Once liquefied it solidifies in nodules in the space between the intermediate and cold end baskets. The result has been increased pressure drop and eventual plugging. Off-line water washings are necessary to remove the soluble deposits. Cold end steam sootblowers are not generally effective in reaching and removing these deposits on-line.

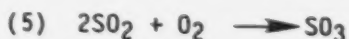
To alleviate this problem NH₃ slip limits of 3 ppm to 5 ppm plus redesign of the air heater are required. Figure 2 shows the redesigns for low and high

sulfur coals. Note that the intermediate and cold end baskets in Figure 2 were made into a single element in the SCR application. Heavier gauge and corrosion resistant materials are used in all sections. Also cold end notched flat (NF) element design (see Figure 3) is used in the combined intermediate/cold end baskets. This design provides less effective heat transfer than the double undulated (DU) element (see Figure 3) design normally used in the intermediate baskets, and hence the combined section is longer than the combined, separate intermediate and cold end sections. However, the more open NF design reduces the adverse deposition effects, and the combined basket allows ammonium bisulfate liquids to run to the base of the element where the deposits can be reached by the sootblower.

The EPRI Arapahoe Test Facility results indicate air sootblowing is not effective in cleaning the ammonium bisulfate deposits. Dry steam (i.e., superheated) sootblowing is required on both ends of the air heater. Vertical shaft air heaters, normally used on coal-fired units, affect drainage when washing the air heater off-line. On-line washing is difficult and requires load reductions.

SULFUR DIOXIDE (SO₂) TO SULFUR TRIOXIDE (SO₃) CONVERSION

The SCR catalyst used to control NO_x also catalyzes SO₂ to SO₃ in the presence of oxygen (see Equation (5) below).



This conversion rate can range from 1 percent to 3 percent. However, most manufacturers strive to control the conversion rate to one percent and this low level should be specified in a purchase specification for this process. SO₃ formation is a function of the initial SO₂ concentration, space velocity and process temperature. High temperatures (e.g., 720°F) and low space velocities (e.g. 2000 hr⁻¹ to 2500 hr⁻¹) promote SO₃ formation.

It is important to note as the SO₃ concentration increases in the flue gas, so does the acid (i.e., H₂SO₄) dew point. Hence, SO₃ increases due to SCR catalyst can require higher air heater exit temperatures and decreased boiler efficiency.

Increased leakage can be caused by the higher differential pressure across the air heater induced by the SCR system. This induced SCR draft loss generally ranges between 6 in. w.g. and 8 in. w.g. The overall effect of increased air heater outlet temperature and leakage is that the volumetric flow could increase 3 to 10 percent with comparable increase in the cost of downstream equipment (e.g., electrostatic precipitator, Induced Draft fan, SO₂ scrubber and chimney).

CATALYST CONSIDERATIONS

CATALYST CONFIGURATION

The catalyst used in this process is generally a vanadium compound impregnated on a honeycomb substrate. The honeycomb grids are designed to allow the passage of coal ash without poisoning or plugging the catalyst bed. The flue gas from coal-fired boilers passes vertically downward through the catalyst bed and ash hoppers are required to collect ash fallout (see Figure 4). It has been determined in Japan, that a particulate control device upstream of the catalyst reactor is detrimental to catalyst activity because the resulting fine particles tend to accumulate in the catalyst pores and limit and/or deteriorate its activity. "Coarse" ash scours the surface thereby maintaining the cleanliness

and high catalyst activity. In order to insure that the leading catalyst elements will not be severely eroded, a dummy layer (see Figure 4, vertical flow) is used at the flue gas entrance to absorb the erosion effects and to streamline the flow. Finally, the catalyst must be tightly sealed to the reactor housing to minimize flue gas bypass in order to maintain high NO_x reduction efficiency and minimize NH_3 slip.

Low dust concentration fuels (i.e., natural gas, distillate oil) use the horizontal flow configuration shown in Figure 4. The hoists for catalyst replacement and the independent support structure for each of the reactors as shown in Figure 4 are required for all fuels.

CATALYST CONCERNS

The catalyst's performance will decrease if poisoning occurs. SO_3 adsorption and ammonia-sulfur compound fouling are two potential causes of catalyst poisoning. Both may be temporary reversible conditions and depend on reaction temperatures. If the reaction temperature falls below the set limits of 580°F for low and medium sulfur coals, and 650°F for high sulfur coals then catalyst activity will be reduced. The reduction amount depends on the frequency and duration of occurrences. In the case of low and medium sulfur coals, poisoning (due to NH_3 and SO_3 fouling) effects can be reversed, if the process operation below 580°F has not exceeded a 12-hour continuous duration by increasing the reactor temperature to 670°F . Extended low temperature operation will lead to permanent catalyst damage.

Reactor operation above 750°F for any coal causes a catalyst material phase transition which reduces catalyst pore volume and total surface area, and causes catalyst activity deterioration. Catalyst deterioration caused by phase transition is irreversible.

Permanent catalyst poisoning can also occur from alkaline metals and trace elements found in the coal or from sulfur oxides in the flue gas. Temperatures below 400°F and moisture condensation may cause permanent poisoning from sufficient concentrations of alkaline metals and acidic attack when combined with sulfur oxides in the flue gas. Within normal reactor temperature operating ranges, permanent ash poisoning and acid attack should not occur. It is recommended that the reactors be purged of the flue gas at boiler shutdown to avoid these problems during catalyst cooling.

The presence of oil and/or oil mist in the reactor should be avoided. This can mask the catalyst surface and deteriorate its performance. Thus this concern can be overcome by bypassing the reactor when starting up on oil and when firing oil at very low loads.

CATALYST LIFE AND COST IMPACTS

Catalyst deactivation occurs gradually and results from poisoning by alkaline metals and/or plugging of micropores by fine particulate matter. Since this gradual deterioration is normal, the initial performance of the SCR systems must exceed the guarantee requirements. As the catalyst activity decreases the $\text{NH}_3:\text{NO}_x$ mole ratio must increase to insure required NO_x reductions are achieved. Hence, there will be corresponding increase in unreacted ammonia due to catalyst deactivation. When NH_3 conversion (see NO_x Reduction/Ammonia Conversion below) and NO_x removal guarantees cannot be achieved simultaneously, then the catalyst life has expired and replacement is required. Catalyst life is generally specified at one year, but manufacturers expect a 2 to 3 year life.

AMMONIA SLIP

SPACE VELOCITY/AMMONIA SLIP

The variables used to design the catalyst bed are space velocity and linear velocity which are derived from the numerical ratio between the gas flow rate and catalyst volume and frontal area, respectively, as shown below.

$$(6) \text{ Space Velocity (SV), hr}^{-1} = \frac{\text{Gas Flow, SCFH}}{\text{Catalyst Bulk Volume, ft}^3}$$

$$(7) \text{ Linear Velocity (LV), Sft/sec} = \frac{\text{Gas Flow, SCFS}}{\text{Catalyst Frontal Area, ft}^2}$$

The limit placed on the NH_3 slip for the initial NO_x concentration are the key design parameter in sizing the catalyst rather than the NO_x reduction requirements. Japanese experience has shown that substantially lower space velocities, 2500 hr^{-1} to 2000 hr^{-1} are required to achieve low NH_3 slip (i.e., 3 to 5 ppm) and thereby minimize air heater plugging. Three years ago space velocities in excess of 3000 hr^{-1} could be used to achieve 90 percent NO_x reduction. Today higher catalyst volumes are required and correspondingly higher process capital and operational costs will result. Previously 10 ppm was assumed in many capital cost analyses (e.g., Reference 1) and hence the cost estimates for SCR systems must now be updated.

Linear velocities ranging between 8 Sft/sec and 9 Sft/sec are used to maintain high process efficiencies.

It is important to note that at higher temperatures (i.e., 700°F) the SCR process is more efficient than at low temperatures (i.e., 600°F). As load drops, the economizer exit temperature drops, and a 600°F economizer exit temperature can be expected between 50 percent to 60 percent load. However, the NO_x reduction efficiency of the process is somewhat maintained at this low temperature because the relative space velocity increases due to the lower flue gas flow rate to offset the lower reaction rate.

NO_x REDUCTION/AMMONIA CONVERSION

NH_3 slip depends on process space velocity, $\text{NH}_3:\text{NO}_x$ molar ratio, temperature and inlet NO_x concentrations. Hence it is interrelated NO_x reduction efficiency. Figure 5 shows NH_3 slip as a function of space velocity and inlet NO_x concentration. Lower space velocities and NO_x inlet concentrations tend to reduce slip. A space velocity of 2500 hr^{-1} or less is generally required to control NH_3 slip below 5 ppm, but NO_x inlet concentrations above 600 ppm would require even lower space velocities than shown. A Japanese regenerative air heater manufacturer recommends that slip levels be held at 3 ppm or less to prevent plugging in the modified designs discussed earlier. Figure 6 expresses NH_3 slip as a function of NH_3 conversion and NO_x inlet concentration. To achieve 3 ppm, 99.5 percent plus NH_3 conversion is required for 600 ppm NO_x . For the higher NO_x inlet concentrations, near 100 percent NH_3 conversion is approached. In these cases, combustion modification may be required reduce initial NO_x concentrations so that SCR can control NH_3 slip to 3 ppm to 5 ppm.

NH_3 slip begins to increase dramatically at $\text{NH}_3:\text{NO}_x$ molar ratios above 0.8 for the high space velocities, and 0.9 for the low space velocities (See Reference 3). This is one reason why the practical upper limit of SCR NO_x

reduction is 80 percent on coal-fired units and why 80 percent NO_x reduction is the accepted practice in Japan.

The process temperature also affects NO_x slip, and at lowest temperatures at lower loads NH₃ slip can be expected to increase somewhat even with the relative increase in space velocity. Hence NH₃ slip limitations should be specified for high and low loads when specifying and/or designing an SCR system.

JAPANESE SCR EXPERIENCE -- COAL-FIRED UNITS

Table 1 shows the new coal-fired utility units equipped with SCR up to early 1987, and SCR retrofits planned through early 1985. Twenty-eight units are listed in all, the largest single SCR application is the 700 MW Takehara 3 and the largest retrofit installation is 265 MW, Yokosuka 2. A total SCR installed capacity of 5225 MW for both new and retrofit applications is indicated. Hence, the Japanese are moving ahead with coal-fired installations. It is very important to note these units fire Japanese, Chinese and Australian coals. Specific use of SCR on U.S. coal-fired units is heavily dependent upon the wide variety of coal ash properties of U.S. coals. Thus Japanese experience is not automatically applicable on U.S. coal-fired boilers. SCR activity in this country is limited to test and pilot facilities which are listed in Table 2.

SCR COST REVIEW

SCR SYSTEM SCOPE OF SUPPLY AND COST COMPONENTS

In order to properly estimate complete SCR capital costs, the systems and equipment which must be provided for a complete SCR system are outlined below, based on the typical arrangement shown in Figure 7.

- NO_x Control Reactor(s) - Each reactor consists of an insulated and lagged carbon steel shell, catalyst cells, catalyst installation and maintenance equipment, sootblowing equipment, inlet and outlet ducts with metallic expansion joints and turning vanes, ash hoppers with flanges and all related structural steel.
- Flue Gas Transition Ducts - This equipment group includes the inlet duct transition from the boiler economizer outlet to the SCR reactor inlet ducts, the outlet transition duct from the SCR reactor outlet duct to the regenerative air heater inlet duct and the SCR reactor bypass duct. The scope of supply also includes all required metallic expansion joints and dampers.
- Ammonia Injection - This equipment group consists of the ammonia vaporizers, the ammonia/air mix chambers, ammonia/air mixture transfer ducting, ammonia/air injection header and nozzle system attached to the economizer outlet ducting, and all necessary ammonia feed and injection controls.
- Ammonia Receiving and Storage - This system includes all pumps, piping and safety equipment required to receive ammonia by truck and then pump the liquid ammonia to the ammonia vaporizer. The ammonia is stored in 30-day storage tank(s).
- Control Panel NO_x Control System - The control panel is located in the boiler control room. The control panel is semigraphic with status lights, panel mounted controllers, captioned annunciator panels; control console and trend/event are tied into the plant's main

computer. Process conditions are reported to the control panel from the primary control element/transmitter devices and the responding control signals are returned to the control devices such as valve/damper positioners or motor control circuits.

- Continuous Emissions Monitors and Recorders - Each train is generally equipped with an inlet and outlet chemiluminescence NO_x monitor, a NH₃ flow recorder, differential pressure recorder, temperature recorders, and oxygen monitors at the inlet and outlet. An NH₃ monitor is desirable at the outlet.
- Economizer Bypass (optional as required) - The economizer bypass ductwork flue gas and flue control damper are generally supplied with the steam generator. The temperature control equipment, i.e., the damper, primary control elements, drivers, etc., is generally provided by the SCR reactor(s) supplier.
- Monorails and Manual Trolleys - Monorails should be located above all equipment to be handled, and are necessary for the removal and replacement of catalyst elements.
- Supporting System Equipment - Such as ash handling equipment for the SCR reactor(s) ash ducts, fire protection, condensate and steam piping to and from the plant, and air ducting for dilution air from the forced draft fans.
- Incremental Induced Draft ID Fan Costs - Increased ID fan costs required to support typically 6 inches w.g. draft loss induced by the SCR reactors and the associated ducting.
- Earthwork Preparation and Foundations Estimate - These costs are generally never included in the vendor's scope of supply.

It is important to note that the total cost of the equipment listed above does not represent the installed cost of the SCR system. Construction labor, engineering, support facilities, and owner's costs must be included in total plant cost.

Once the total plant cost is established a contingency must be added to these costs which ranges from 10 percent to 35 percent depending upon the confidence of the estimate and the certainty that the process will perform as expected with little or no modification after installation. Finally, escalation and interest during construction costs must also be added to total plant costs.

SCR CAPITAL COSTS -- PULVERIZED COAL-FIRED UTILITY BOILERS

The total capital costs of an SCR system on a new coal-fired unit (See Figure 7) was estimated for a eastern U.S. utility firing a medium sulfur coal (i.e., less than 2000 ppm SO₂) and for a retrofit on a PC unit firing western low sulfur coal. It should be noted that maximum coal sulfur content which has been used in conjunction with an SCR is 1.7 percent. Hence, higher contingencies should be used for coal higher sulfur coal applications. Table 3 indicates the capital cost estimates prepared using the EPRI economic guidelines (Reference 4). Note the variation in space velocity for the retrofit cases.

The new unit SCR costs in Table 3 reflect the higher costs of the SCR system due the devaluing of the dollar against the yen (i.e., now 150 yen = 1 dollar). This impacts only the reactor and catalyst cost because the remaining scope of

supply is purchased in the U.S. Table 3 also reflects a retrofit cost variation of approximately 20 to 30 \$/kW and a 37 \$/Kw cost penalty for lowering the space velocity from 3160 hr⁻¹ to 2000 hr⁻¹. For estimating purposes this latter differential may be interpolated between the space velocity values.

The overall costs of the retrofit cases in Table 3 are shown in Table 4 and Table 5 shows percentage comparisons of these cases from 3 different aspects. It should be noted that the present worth of revenue requirements (PWRR) increases significantly as the space velocity decreases, but decreases markedly as life increases. It is clear that the increasing life decreases the levelized annual operating costs and that the increase in catalyst cost from the higher to the lower space velocity is very pronounced. Hence, the initial catalyst cost, the catalyst replacement cost and catalyst life are the main economic concerns and drivers of SCR process economics. Finally, it should be noted that the two year catalyst life drops the levelized cost of power 25 to 28 percent, but the increased volume of catalyst due to a change in space velocity from 3160 hr⁻¹ to 2000 hr⁻¹ raises the levelized power cost 35 to 42 percent.

SCR COSTS-INDUSTRIAL BOILERS

On November 25, 1986, Federal Industrial New Source Performance Standards were promulgated for industrial boilers having a fuel input ranging greater than 100 MBTU/Hr but less than 250 MBTU. These "standards apply to all new, modified, or reconstructed steam generating units with a heat input greater than 29MW (100 MBTU/Hr) for which construction is commercial after June 19, 1984 except for electric utility steam generating units covered by 40 CFR Part 60 Support Da." The NO_x limits set forth by the new regulation are shown in Table 6.

In addition to units above 100 MBTU/Hr, units with less than this input may be susceptible to Best Available Control Technology (BACT) under Prevention of Significant Deterioration (PSD) provisions of the Clean Air Act when they are part of a facility which will emit greater than 100 tons of NO_x per year to the atmosphere. Owners may also review the use of SCR on small boilers when attempting to install them in non-attainment areas, and at the same time attempting to minimize off-set requirements. Therefore, a brief example of SCR impacts on the industrial user are reviewed in this paper. This example is a modified adaptation of an actual study.

One industrial user was faced with performing a BACT analyses for NO_x control on a steam generator which he wished to install. For purposes of this analysis, BACT was defined as installing and operating a steam generator such that NO_x emissions are reasonably minimized. However, there are several qualifiers for BACT, these are:

- 1) The NO_x control technology used should be feasible and commercially proven.
- 2) The NO_x control technology should not disrupt or cause the steam generator to be ineffective in meeting its process objectives.
- 3) The NO_x control technology must be cost effective, that is, it must not increase the capital and/or operational costs of the process, to the point where the process becomes non-competitive and/or cost prohibitive.

This latter requirement is consistent with the spirit and intent of the new Industrial NSPS. Quoting 40 CFR Part 60, November 25, 1986, "These standards being adopted today were found to have no significant adverse economic impacts on any of these industries."

Three NO_x control alternatives were reviewed for a natural gas-fired steam generator. There were 1) a low heat release boiler without modification; 2) flue gas recirculation (FGR) and; 3) SCR. The steam generator is equipped with a full economizer for heat recovery with and without FGR. When an SCR is considered, economizer surface must be removed to achieve a boiler outlet temperature of 720°F. In this case, an air heater is cost effective for energy recovery because otherwise an approximate 10 percent drop in boiler efficiency would be incurred. Table 7 provides the technical and cost data and, Table 8 provides economic comparison data for the three alternatives.

It appears that the increased cost of steam is negligible even for the SCR alternative. However, this is not the case because the present worth differential of the SCR is \$1.426 million which is about four times the cost of the original boiler, and the average differential NO_x control cost is 4667 \$/ton and the incremental NO_x control cost for SCR versus FGR is 11,916 \$/ton. The original boiler had a low heat release furnace and emits 0.1 lb/MBTU consistent with NSPS requirements for natural gas (See Table 6). In the future several thousand boilers of this size could be installed in the U.S. Considering the present worth of the SCR in Table 8, this reflects several billion dollars which the public will pay to accommodate SCR in small industrial boilers. This makes the SCR not cost effective and it therefore does not meet the BACT requirement 3 listed above. Other combustion modification techniques would be considered before SCR, such as flue gas recirculation for NO_x control on industrial boilers, because of its cost effectiveness as shown in Table 8. However, the near 50 percent NO_x reduction using FGR must be verified. SCR should be the last resort.

CONCLUSIONS

This update provides several technical and cost considerations which will impact the application of SCR technology in the United States, and these are:

- SCR is now being applied to new and existing Japanese coal-fired units. The largest retrofit unit is 265 MW, and the largest new unit application is 700 MW.
- The Japanese units fire indigenous, Chinese and Australian coals which means this experience may not be extrapolated to U.S. units firing a wide variety of coals, particularly those with higher sulfur concentrations. Ash particle size and trace element constituents determine the applicability of SCR to a specific coal. Hence, SCR still must be technically proven on U.S. coals.
- Ammonia slip has become a prime technical concern for this process because NH_3 combines with SO_3 (see equation (5)) to form ammonium bisulfate which plugs air heaters. Japanese experience has indicated that this slip must be limited to 3 ppm to 5 ppm, and the standard regenerative air heater must be redesigned to limit the plugging problem.
- In order to reduce ammonia slip it will be necessary to reduce space velocities from the 3000 hr^{-1} required for high NO_x reduction efficiency to 2500 hr^{-1} to 2000 hr^{-1} . This means the catalyst

volumes will now be dictated by NH_3 slip requirements rather than NO_x reduction requirements.

- Previous SCR cost estimates based on 10 ppm NH_3 slip correspond to about 3000 hr^{-1} space velocities. The requirements for lower space velocities determines that previous SCR capital (e.g., Reference 1) and operating costs be updated.
- The dollar has devalued appreciably (now 150 yen/dollar) and thus will significantly raise SCR reactor and catalyst costs because the SCR scope items will be purchased from Japanese SCR suppliers. The SCR costs developed in Reference 1 were based on 240 yen/dollar.
- When estimating SCR total capital requirements it is necessary to include all the scope items identified in this paper, as well as labor, engineering, support facility, contingency, escalation and interest during construction costs.
- SCR capital cost for new medium sulfur coal-fired units is now determined to be 141 \$/kW for a 300 MW (net) unit.
- Retrofit costs on 200 plus MW (net) unit for space velocities from 3160 hr^{-1} to 2000 hr^{-1} ranged from 136 \$/kW to 172 \$/kW in 7/1/87 dollars. About 20 to 30 \$/kW of the above costs was required for retrofit considerations. A 37 \$/kW differential cost increase was required to use the lower space velocity (i.e. 2000 hr^{-1}) in this cost comparison.
- Initial and replacement catalyst costs as well as catalyst life are the main economic contributors to SCR cost. A 2 year life reduces the levelized power costs 25 to 28 percent. While a decrease in space velocity from 3160 hr^{-1} to 2000 hr^{-1} raises levelized power costs 35 to 42 percent.
- In the industrial boiler case, the present worth of an SCR would be approximately 4 times the original boiler costs. When several thousand small boilers were considered it is noted that a several billion dollar economic impact could be assessed for SCR control. Combustion modification is still the most cost effective means of NO_x control.
- The main argument against the use of SCR in this country is its high cost. Ammonia slip requirements of 3 ppm to 5 ppm, based on Japanese experience, will raise SCR reactor, catalyst, and air heater costs and hence SCR process costs over estimates of 3 years ago. This further mandates the use of cost effective combustion modification technologies or techniques for NO_x control in the U.S.

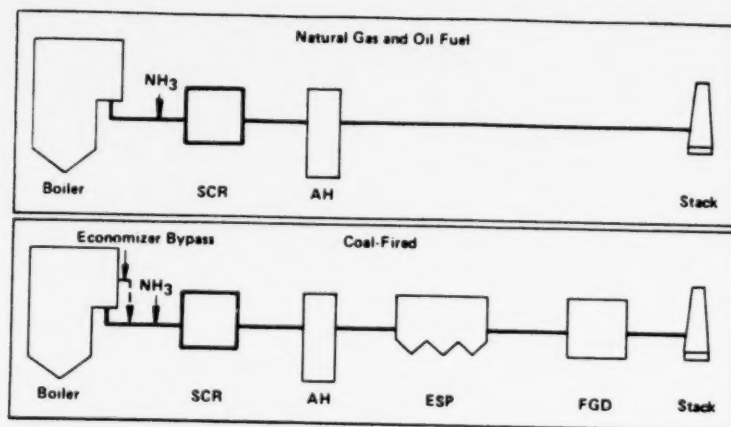
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DISCLAIMER

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.



NOTES: SCR - Selective Catalytic NO_x Reduction System,
 AH - Air Heater,
 ESP - Cold-side Electrostatic Precipitator,
 and FGD-Flue Gas Desulfurization System.

**Figure 1. SCR System Placement
 In Power Plant Flue
 Gas Stream**

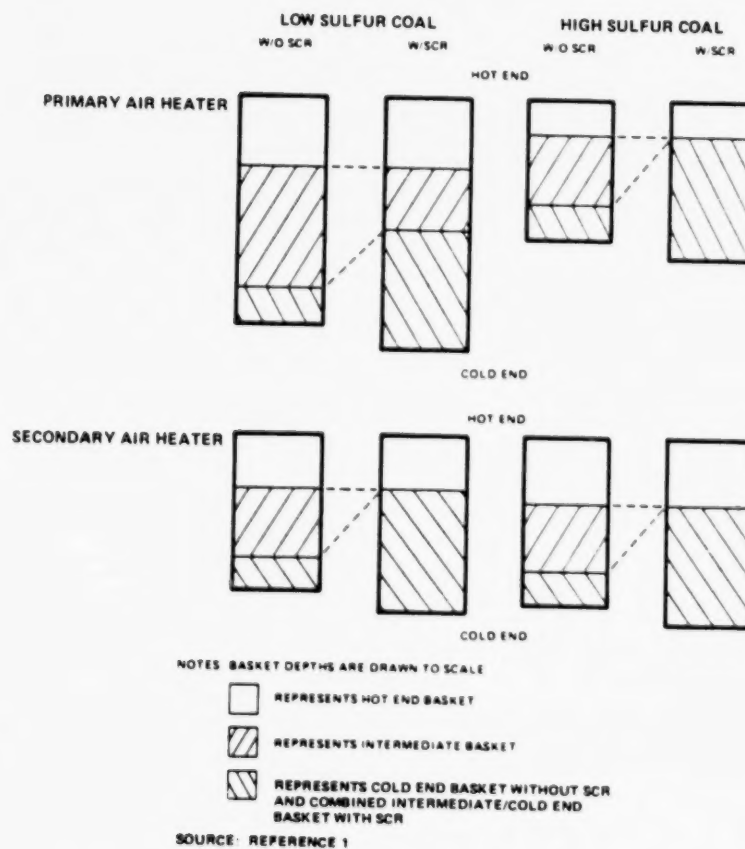
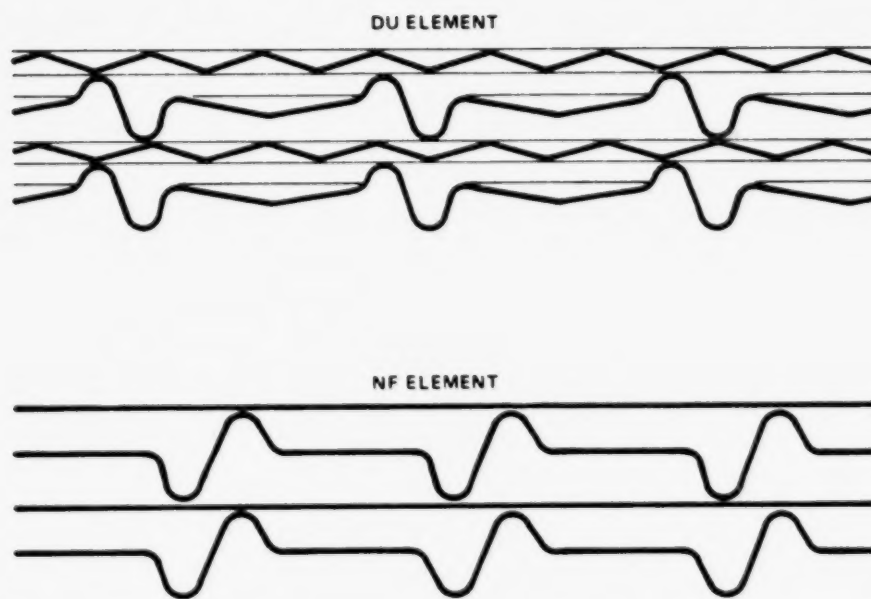
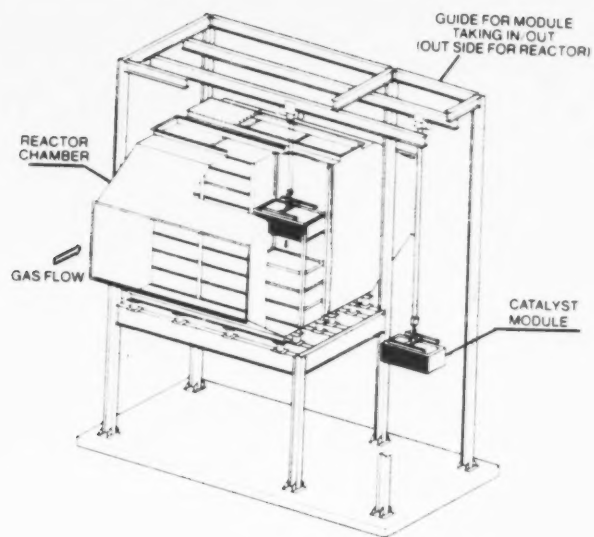


**Figure 2. Regenerative Air Heater Design Modification
 with Selective Catalytic NO_x Reduction for
 Low and High Sulfur Coals**

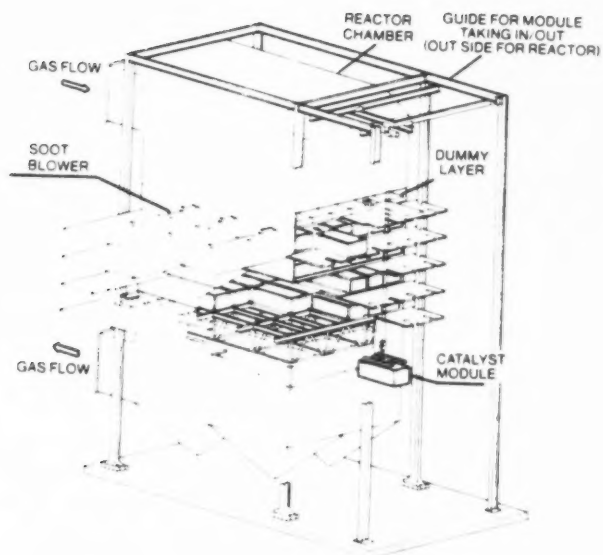


SOURCE: REFERENCE 1

Figure 3. Air Heater Basket Element Design



**Horizontal flow fixed bed type with
honeycomb catalyst
For very low particulate fuels**



**Vertical flow fixed bed type with
honeycomb catalyst
For coal-fired units**

**Figure 4. SCR Catalytic Reactor
Configurations**

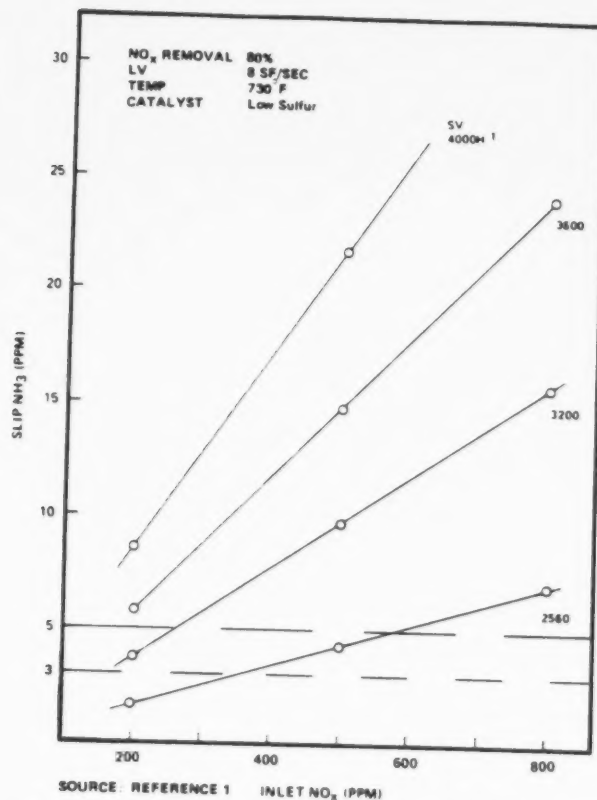


Figure 5. NH₃ Slip Versus Space Velocity and NO_x Concentration

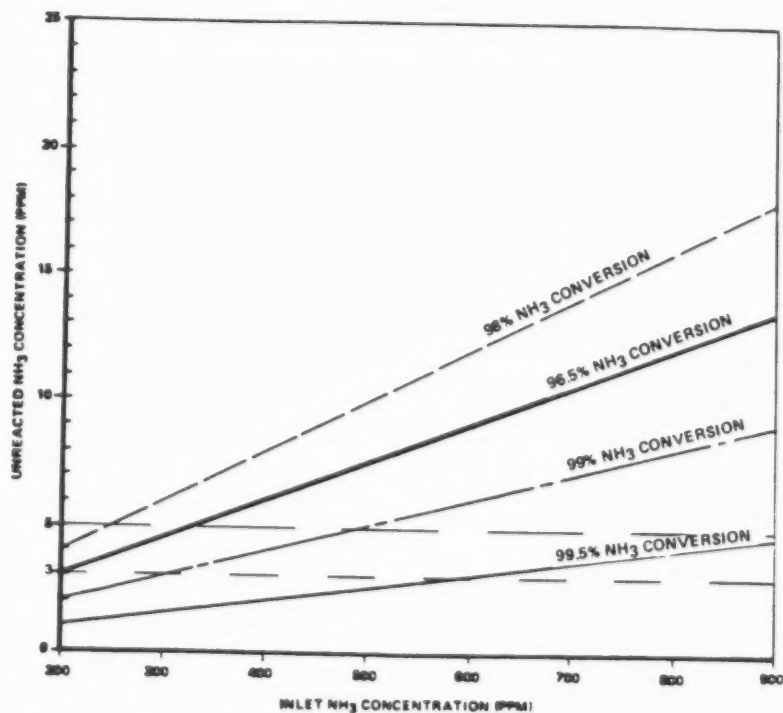


Figure 6. NH₃ Slip Versus NH₃ Conversion Rate and NO_x Concentration

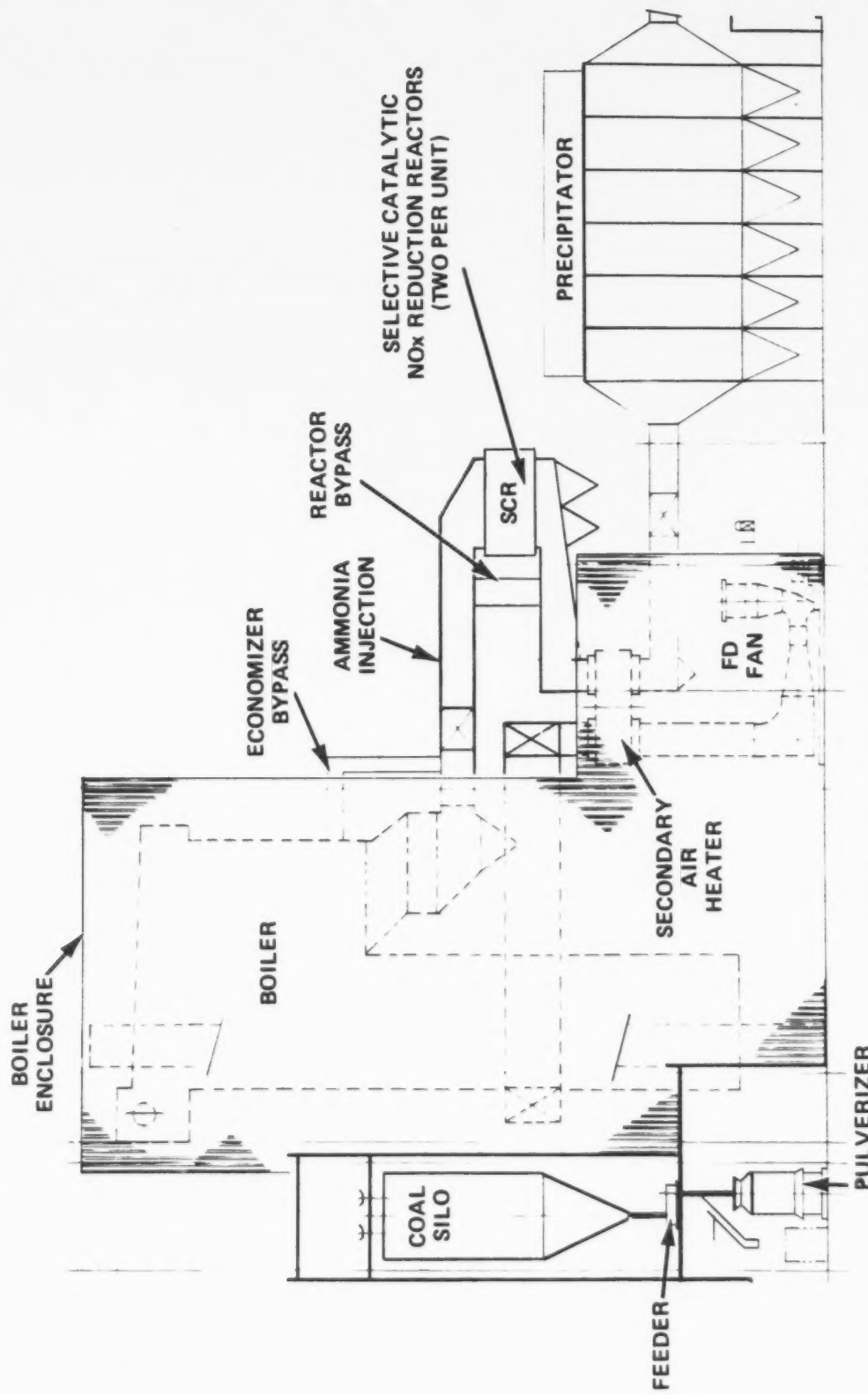


Figure 7. Typical Selective Catalytic Reduction System (SCR) Arrangement for a Pulverized Coal-Fired Boiler

TABLE 1. SCR INSTALLATIONS AND RETROFITS ON COAL-FIRED POWER PLANTS IN JAPAN

<u>Power Company</u>	<u>Station</u>	<u>Unit No.</u>	<u>Unit Capacity (MW)</u>	<u>NO_x Reduction (%)</u>	<u>NH₃ Slip (%)</u>	<u>Catalyst Life (years)</u>	<u>Commercial Date (years)</u>
SCR Installations on New Units							
Hokkaido	Tomato-Azumi	1	88	80	10	1	10/80
Jooban	Nakoso *	8	600	50	--	--	1/83
EPDC	Takehara	3	700	80	2.6	2	3/83
Jooban	Nakoso *	9	600	29	5	2	4/83
Kyodo	Sakata	1	350	35	5	--	6/84
Kyodo	Sakata	2	350	35	--	--	5/85
Chugoku	Shin-Onoda	1	500	80	5	?	4/86
Chugoku	Shin-Onoda	2	<u>500</u>	80	5	1	2/87
Total			3688				

SCR Retrofits on Existing Units

Chugoku	Shimonoseki	1	175	50	--	--	5/80
EPDC	Takehara	1	125	80	5	2	7/81
EPDC	Takehara	1	125	80	5	2	7/81
Chugoku	Shinube *	3	156	65	--	--	2/82
Chugoku	Shinube *	2	75	65	--	--	3/82
Chugoku	Shinube *	1	75	65	--	--	5/82
Kansai	Himeji *	1	33	80	5	1	9/82
Tohoku	Sendai *	2	175	60	5	1	3/83
Tohoku	Sendai *	3	175	60	5	1	3/83
Kyushu	Minato *	1	156	53	--	--	4/83
Shikoku	Saijo *	1	156	65	--	--	7/83
Shikoku	Saijo *	2	250	65	7	1	1/84
Chugoku	Mizushima *	1	125	65	5	1	7/84
Chugoku	Mizushima *	2	156	65	5	1	7/84
Toyama	Toyamashinko	1	200	60	5	1	11/84
TEPCO	Yokosuka	1	265	70	--	--	11/84
Toyama	Toyamashinko	2	200	60	5	1	12/84
TEPCO	Yokosuka	2	<u>265</u>	70	--	--	2/85
Total			2887				

Total New and Retrofit: 5225

* These units are capable of operating on oil and/or coal. However, what fraction of the time and/or power generation is for coal is unknown.

TABLE 2. U.S. SCR TEST FACILITIES

<u>Name</u>	<u>Location</u>	<u>Fuel</u>	<u>Size</u>
Arapahoe Test Facility	Colorado	Western U.S. Coal	2.5 MW
Huntington Beach Power Plant	California	Oil, N. Gas	107.5 MW
Mitchell Power Station	Georgia	Eastern U.S. Coal	0.5 MW

TABLE 3. SCR INSTALLATION COSTS (80% NO_x REDUCTION)
(7/1/87 U.S. DOLLARS)

	Medium Sulfur New Unit ¹ 300 MW Net SV ³ -2500 Hr ⁻¹ \$/kw	Low Sulfur Retrofit Unit ² 200 MW Net Plus SV ³ -3160 Hr ⁻¹ \$/kw	SV ³ -2000 Hr ⁻¹ \$/kw
Reactor System	57.6	54.7	78.7
Ducting	8.5	4.8	4.8
NH ₃ Storage	7.6	10.9	10.9
Control System/Monitors	4.8	5.8	5.8
Induced Draft Fan Differential	2.0	6.8	6.8
Air Heater Differential	3.8	NA ⁴	NA ⁴
Ash Handling	NA ⁴	1.3	1.3
Demolition/Relocation	--	0.6	0.6
General Facilities	1.3	1.2	1.2
Total Process Capital	84.3	86.1	109.2
General Facilities	8.6	--	--
Engineering/Home Office Fees	8.0	8.1	10.3
Project Contingency ⁵	14.6 (17)	17.2 (20)	21.8 (20)
Process Contingency ⁶	8.1 (9.5)	9.0 (11)	12.0 (11)
Total Plant Cost	123.6	120.9	153.3
AFDC ⁷	13.9	13.2	16.7
Total Plant Investment	137.5	133.7	169.5
Regulatory Allowance	0.4	0.3	0.3
Preproduction Cost	2.3	1.7	1.7
Inventory Capital	0.4	0.3	0.3
Total Capital Requirement	140.6	136.0	171.8

- 1 The new unit reactor costs reflect the current exchange rate of 150 yen = \$1.
2 Retrofit cases reflect past exchange rates.
3 SV - Space Velocity
4 NA - not available
5 The number in () is the percent project contingency.
6 The number in () is the percent process contingency
7 AFDC - Allowance for funds during construction.

TABLE 4. SCR COST COMPARISONS - U.S. DOLLARS
(200 MW NET PLUS UNIT RETROFIT CASES)

Company Factor, %	65	65	65	65
NO _x Reduction, %	80	80	80	80
Maximum NH ₂ Slip, ppm	10	3	10	3
Space Velocity, hr ⁻¹	3160	2000	3160	2000
Catalyst life, years	1	1	2	2
Capital Cost, \$/Kw	136.0	171.8	136.0	171.8
Annual Operating cost, M\$/yr (7/1/88)	6052	9111	3630	5180
PWRR (7/1/87), M\$	113	159	85	114
First Year, Mills/KwHr	9.0	12.5	7.1	9.4
Levelized, Mills/KwHr (7/1/87)	11.7	16.6	8.8	11.9

NOTES: 1) Escalation - 6%.
2) MAR - 12%.

3) FCR - 18%.
4) Remaining Life - 20 years.

TABLE 5.* SCR COST COMPARISONS - PERCENTAGE
(200 MW NET PLUS UNIT RETROFIT CASES)

	<u>Base</u>	<u>Alt. 1</u>	<u>Alt. 2</u>	<u>Alt. 3</u>
Space Velocity, Hr ⁻¹	3160	2000	3160	2000
Catalyst Life, Years	1	1	2	2
Capital Cost, %	100	126	100	126
Annual Operating Cost, %	100	151	60	86
PWRR, %	100	141	75	101
First Year, Mills/KwHr, %	100	139	79	104
Levelized, Mills/KwHr, %	100	142	75	102

	<u>Base 1</u>	<u>Alt. 1</u>	<u>Base 2</u>	<u>Alt. 2</u>
Space Velocity, Hr ⁻¹	3160	2000	3160	2000
Catalyst Life, Years	1	1	2	2
Capital Cost, %	100	126	100	126
Annual Operating Cost, %	100	151	100	143
PWRR, %	100	141	100	134
First Year, Mills/KwHr, %	100	139	100	132
Levelized, Mills/KwHr, %	100	142	100	135

	<u>Base 1</u>	<u>Alt. 1</u>	<u>Base 2</u>	<u>Alt. 2</u>
Space Velocity, Hr ⁻¹	3160	3160	2000	2000
Catalyst Life, Years	1	2	1	2
Capital Cost, %	100	100	100	100
Annual Operating Cost, %	100	60	100	55
PWRR, %	100	75	100	72
First Year, Mills/KwHr, %	100	79	100	75
Levelized, Mills/KwHr, %	100	75	100	72

* Refer to Table 4, all cases at 65% capacity factor and 80% NO_x reduction.

TABLE 6. INDUSTRIAL NSPS NO_x EMISSION LIMITS (1)

	<u>NO_x Limit</u>
(1) Natural Gas and distillate oil except(4)	
(i) low heat release(2)	43 (0.10) ⁴
(ii) high heat release(3)	86 (0.20)
(2) Residual Oil	
(i) low heat release	130 (0.30)
(ii) high heat release	170 (0.40)
(3) Coal	
(i) Mass feed stoker	210 (0.50)
(ii) spreader stoker and fluidized bed combustion	280 (0.60)
(iii) pulverized coal	300 (0.20)
(iv) Lignite except (v)	280 (0.60)
(v) Lignite mined in North Dakota, South Dakota, or Montana, and combusted in a slag top furnace	340 (0.80)
(4) Duct burner used in a combined cycle system	
(i) natural gas or distillate oil	86 (0.20)
(ii) residual oil	170 (0.40)

Notes: 1) See November 25, 1986 Federal Register, Part V, EPA, 40 CFR, Part 60.
2) Less than 70,000 Btu/ft³-hr
3) Greater than 70,000 Btu/ft³-hr
4) The first value is NO_x emission limits on nanograms per joule heat input, the values in () are in lb/MBtu.

TABLE 7. INDUSTRIAL STEAM GENERATOR
(LOW HEAT RELEASE FURNACE)
NO_x CONTROL COMPARISONS

	No Modification (Base Case)	W/FGR	W/SCR
Steam Generator, lb/hr	82,500	82,500	82,500
Natural Gas Input, MBTU/Hr	100	99.2	100
<u>Economizer Outlet</u>			
SCFM(1)	19,190	19,000	19,190
ACFM	29,640	29,340	46,020(2)
Actual Temp. °F	300	300	720(2)
<u>NO_x Emissions</u>			
ppm at 2% O ₂ dry	85	42.0	15.3(3)
lb/MBTU	0.10	0.0495	0.018
tons/year(4)	43.8	21.7	7.9
<u>Capital Costs</u> (1/1/87 U.S. \$)			
Steam Generator w/support equipment	362,000	421,000	337,000
SCR	N/A	N/A	445,000
Air Heater	N/A	N/A	229,000
Total	362,000	421,000	1,011,000
<u>Operating Cost</u> (4) (1/1/87 U.S. \$/year)			
Fuel(5)	2,935,000	2,911,000	2,935,000
Energy-KwHr(6)	5,000	29,000(7)	11,000
Ammonia(8)	N/A	N/A	3,000
Catalyst(9)	N/A	N/A	49,000
Total	2,940,000	2,940,000	2,998,000

- NOTES: (1) At 32°F, 147 psia
 (2) At economizer outlet, an air heater outlet temperature of 300°F is assumed
 (3) Assumes 82% NO_x reduction with a NH₃:NO_x molar ratio of 0.89%
 (4) Based on a 100% percent capacity factor
 (5) Fuel cost is 3.35 \$/MBTU
 (6) Energy cost is 4¢/KwHr
 (7) Due to power cost of flue gas recirculation fan and increased forced draft power requirements
 (8) Ammonia cost is 170 \$/ton
 (9) Based on a catalyst SV of 11060 hr⁻¹ noting that this catalyst is different from a catalyst used for a coal-fired boiler. Assumes NH₃ slip limit of 5ppm, and a 2 year catalyst life, with half the catalyst cost shown above.

TABLE 8. INDUSTRIAL STEAM GENERATOR ANNUAL COST(1) COMPARISON
(All COSTS IN 1/1/87 U.S. \$(2))

	<u>No Modification</u> (Base Case)	<u>With FGR</u>	<u>with SCR</u>
Annual Steam Generation, 1,000 lb/yr	722,700	722,700	722,700
NO _x tons/year	43.8	21.7	7.9
Annual Capital Cost	46,000	49,000	119,000
Annual Operating Cost	2,940,00	2,940,000	2,998,000
Total Annual Cost	2,986,000	2,989,000	3,117,000
Differential Annual Cost	0	3,000	131,000
First Year Cost \$/1000 lb/steam	4.132	4.136	4.313
First Year Differential NO _x			
Control Cost, \$/ton NO _x	---	138.0	3,649
Differential Present Worth	---	26,000	1,426,000
Levelized Differential Annual Cost	---	3,055	167,500
Levelized Differential Cost			
Steam \$/1000 lb	---	0.4	23.2
Levelized Differential Cost			
\$/ton NO _x Reduced	---	138.2	4,667
Incremental NO _x Reduction			
tons/year	Base	22.1	13.8
Incremental Levelized Annual Cost	Base	3,055	164,445
Incremental Levelized Annual Cost,			
\$/ton NO _x Reduced		138.2	11,916

- Notes: (1) Economic parameters
Interest Rate - 10 percent
Escalation Rate - 6 percent
Remaining Life - 20 years
(2) Based on a 100 percent capacity factor.

MECHANISMS OF FIXED NITROGEN REDUCTION IN
PULVERIZED COAL FLAMES

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ABSTRACT

Although the major features that mark the conversion of coal nitrogen have been identified through extensive research, some portions of the process are not well understood. An understanding of these processes, and their associated rates, will provide the information needed to develop process models. Three areas have been identified for which present process models fail to predict the observed fixed nitrogen reduction. These include (1) the reduction in nitrogen that occurs at very short times, including devolatilization and reaction in the immediate vicinity of the coal particle, (2) nitrogen reduction in the bulk fuel-rich regions that are characteristic of staged combustion and reburning applications, and (3) fixed nitrogen reduction at the final leaning-out point. The work reported here examines these problems through a task on homogeneous kinetics, a task on NO reduction by heterogeneous media, and a task examining the overall process of fixed nitrogen reduction in direct coal combustion.

INTRODUCTION

The details of nitrogen chemistry in coal flames have received considerable research attention in recent years. The work has focused on both understanding the fundamentals, and developing means of reducing NO_x emissions. These efforts have resulted in a good overall understanding of the general outline of nitrogen reactions in coal flames.

One goal of these efforts is the development of process models. These models can ideally be used to predict the performance of existing configurations, optimize processes for NO_x control, and identify potential new approaches to NO_x abatement. However, certain portions of the coal-nitrogen conversion process cannot yet be quantitatively predicted. These include:

1. Short time phenomena: The nitrogen reduction which occurs in the devolatilization region has never been successfully modeled. The reduction is the result of a complex interaction between reaction in the char pores and reaction in the immediate vicinity of the particle.
2. Nitrogen reduction in the fuel-rich zone: In fuel-rich coal combustion fixed nitrogen is reduced, and HCN and NH_3 appear under fuel-rich conditions.
3. Nitrogen reduction at the leaning-out point: Fixed nitrogen is usually reduced at the air staging point in reburning and staged combustion. The homogeneous models do not normally replicate this behavior.

This paper is a report of an ongoing study of each of these issues. The work to date has emphasized fuel-rich reduction, and the bulk of the discussion is on this issue.

PROGRAM APPROACH

If the reaction of coal-nitrogen is followed throughout its history within a boiler environment, the various fundamental processes governing its fate can be outlined. Consider an application of normal staged combustion. The coal particle enters the burner and initially starts to heat in an oxygen-rich environment. The coal chemical matrix will begin to decompose and release primary volatile nitrogen species into secondary products. Some ratio of primary/secondary devolatilization products are eventually released into the gas-phase surrounding the char particle. Here, further reaction is possible in a diffusion flame environment. Eventually the interparticle oxygen is consumed and the remaining fixed nitrogen diffuses throughout the gas medium.

Compared with the short devolatilization time, a relatively long time is spent in the fuel-rich zone. Here, various reactions are capable of reducing fixed-nitrogen to N_2 . Also, NO can be recycled into fixed nitrogen, and even N_2 can become fixed under extreme circumstances. The net result is a decay in fixed nitrogen throughout this zone.

At the lean-out point, oxygen becomes available to oxidize all of the reduced nitrogen species. Normally, a fraction of this is reacted to N_2 .

The following fundamental tools are necessary to replicate the behavior under each of these conditions:

- Nitrogen release rates and speciation from coal. This is the subject of work funded by DOE elsewhere.
- Nitrogen reactions with the char matrix. This also is funded elsewhere by DOE.
- Nitrogen reactions in the coal particle diffusion flame. This will involve the homogeneous chemistry of nitrogen compounds, as well as the hydrocarbon homogeneous chemistry that forms the background against which the nitrogen reactions occur. There is also considerable experimental evidence for the existence of a condensed phase in the region about the coal particle. This raises the possibility that heterogeneous nitrogen reaction may be important.

- Nitrogen reactions in the fuel-rich region. This would consist of both the heterogeneous and homogeneous components identified above.
- Nitrogen reduction at the lean-out point. This is most likely governed strictly by homogeneous chemistry.

Thus, successful modeling of nitrogen reduction in coal flames may require as many as three fundamental elements:

1. Devolatilization/Secondary Char Reaction Element
2. Homogeneous Chemistry Element
3. Heterogeneous Chemistry Element

The first element is being addressed elsewhere. The homogeneous element and heterogeneous element each form a task within the present study. The final task of this study is to obtain nitrogen reduction data from actual coal flames. The purpose of these data are to provide a benchmark to guide and evaluate the contribution of the more fundamental elements.

HOMOGENEOUS CHEMISTRY

APPROACH

The goal of this task is to assemble a gas-phase chemistry package which contains the species and reactions necessary to model homogeneous nitrogen conversion in coal flames. As such, it necessarily has to contain an element that reproduces the hydrocarbon chemistry that forms the background environment against which the nitrogen reactions occur. The key questions that must be addressed in defining a mechanism include:

- Species that must be included
- Sources for reactions and rates
- Form of data against which the mechanism will be tested

Although the experimental definition of reaction kinetics has been underway for many years, the last five to ten years have been particularly productive. New diagnostic techniques, such as laser induced fluorescence, have permitted non-obtrusive measurements of intermediates in flames. Also, new high-speed chemical kinetic algorithms have eased the extraction of individual rate constants from complex flame data. The availability of these data have led a number of groups to become involved in critical evaluation of results, and assembly of the rates into predictive mechanisms.

The focus of the current effort is not to assemble an independent mechanism from the original sources. Rather, the critical compilations are used to provide the basis of the current mechanism. Each reaction from the selected compilations is compared against the corresponding reaction from the other compilations for consistency. The means of comparison is shown in Figure 1. Each rate is submitted to a specialized computer program which provides a Arrhenius plot comparison. A second specialized program calculates the standard forward rate for plotting when only the reverse rate is supplied. This provides a means of identifying significant variations in the way individual reactions are handled between the

various mechanisms. Reactions showing significant deviations are investigated in detail to resolve the discrepancy.

Finally, the assembled mechanism is tested against well characterized flame data involving fixed-nitrogen reduction. The purpose of this exercise is to ensure the kinetics are capable of predicting nitrogen behavior in systems that are sufficiently simple that they can be directly modeled with minimal assumptions. However, these systems must contain all of the chemistry that would be expected to be important in the homogeneous conversion of coal nitrogen. In each case, sensitivity analysis is applied to identify the key reactions controlling the nitrogen behavior. In the event of a significant discrepancy between the model and the data, the sensitivity of the computed results to variations in the key reaction rates is evaluated. The critical question of whether there is sufficient uncertainty in the original rate data to permit the necessary adjustment to merge the data and model results is addressed.

Sources of compiled kinetic data have included Warnatz [1], Westbrook and Dryer [2], Glarborg et al., [3,4], Saliaman and Hansen [5], and a mechanism previously developed at EER [6].

APPLICATIONS

The two applications that are illustrated here are reburning and micro-diffusion flame chemistry during devolatilization.

A large data base has been developed on bench-scale reburning at EER [7]. This forms a convenient basis for evaluating the process in terms of the controlling kinetics. Figure 2 shows the results of direct application of the kinetics to the experimental conditions. Two principal variations between the model and data are noted:

1. The model uniformity predicts less nitrogen reduction than is shown in the experiment.
2. The sharp discontinuity in NO_x reduction near the stoichiometric point is blurred in the data.

The second point can be rationalized in terms of imperfect mixing; the state of the reactor at any given overall stoichiometry will actually consist of some distribution of stoichiometries centered about the mean value. Thus, a sharp distinction based on perfect mixing will become blurred when mixing is imperfect. Both the data and model show a minimum in NO_x emissions at $\text{SR} = 0.9$.

An important use of the model is to answer the questions of what limits NO_x reduction, and how can these limits be overcome. An examination of the principal kinetic pathways shows that the steps illustrated in Figure 3 are predicted to govern the reburning process. The recycling of NO through HCN via reaction with CH_i radicals provides a source of N-atoms. Since these are partially oxidized to NO and partially reduced to N_2 , the greater the extent of the recycle reaction, the greater the reduction of fixed nitrogen. Thus, the influence of stoichiometry on reburning is really determined by two subsidiary questions:

1. How does stoichiometry influence the fate of N-atoms (i.e., N_2 vs. NO)?
2. How does stoichiometry influence the availability of CH_i radicals?

The answer, according to the reaction kinetics, is that CH_i peaks on the rich side of stoichiometric because oxygen atoms are required to produce CH_i from its immediate hydrocarbon precursor, acetylene. As illustrated in Figure 3, under increasingly rich conditions the CH_i yield decreases at the expense of C_2H yields; this species and its products do not activate the recycle reaction. Since the $\text{N} + \text{NO}$ reaction will not depend strictly on stoichiometry (except through the N-atom dependence) it is the competing reaction of $\text{N} + \text{OH}$ that increases in rate when passing from fuel-rich to stoichiometric conditions. Thus, the decrease in CH_i availability limits the reburning reaction on the fuel-rich side of the optimum, and the increased fraction of N-atoms that are converted to NO limits reburning on the lean side.

A second aspect of reburning is illustrated in Figure 4, where NO_x reduction efficiency is compared for a series of fuels. For the hydrocarbon fuels the stoichiometric influence is similar: an NO_x minimum near $\text{SR} = 0.9$, and relatively little change in efficiency with increasingly rich conditions. Use of hydrogen as a reburning fuel yields a continuously increasing reduction efficiency with richer conditions. The kinetics responsible for this behavior are also shown in Figure 3. At progressively richer conditions, recycle is promoted by $\text{NO} + \text{H} + \text{M}$. Since H atom monotonically increases with increasingly fuel-rich conditions, the hydrogen reburning reaction becomes more efficient. One interesting point is that the hydrogen and hydrocarbon mechanisms may complement each other under rich conditions; as SR is decreased, the lower efficiency of the CH_i recycle reaction is partially offset by the increased rate of the $\text{NO} + \text{H} + \text{M}$ reaction. This is indicated to be responsible for the nearly flat response of NO_x reduction efficiency on the rich side of the optimum.

The second application of the kinetics deals with the reduction in fuel-nitrogen that accompanies the devolatilization process. As was mentioned previously, this potentially includes heterogeneous reactions within the coal particle as well as external reactions in the immediate vicinity of the particle.

To examine the second case, a two-dimensional diffusion flame code was configured into spherical coordinates to simulate, in a simplified manner, the diffusion flame that has been observed surrounding devolatilizing coal particles in hot environments [8,9]. This simplified spherical diffusion model uses pyrolysis product distributions from Solomon [10]. The volatile flux rate at the particle surface was determined as a boundary condition by the observed devolatilization rate in the burner [8]. The initial particle temperature was taken as 300 K and the free stream gas corresponded to the equilibrated combustion products at the measured burner temperature of 1250 K. The equilibrium assumption is reasonable for all gases except NO . To avoid contaminating the fuel-nitrogen calculations with free stream fixed nitrogen, the free stream NO was set to zero.

The results showed that a steady state was approached in less than 1 msec. This implied that the observed flames are operating in quasi-steady state. Figure 5 shows profiles near the particles for the various nitrogen series. All go towards zero concentration at the particle surface except the evolving species, NH_3 and HCN . At long distances from the particle all of the intermediates have been consumed, and the NO decrease is due to its steady state diffusion away from the particle source. The NO flux is integrated over the spherical surface at a radius beyond the zone of chemical activity to yield the net NO produced by the single particle. Relating this to the initial release rate of NH_3 and HCN provides an estimate of the amount of nitrogen reduction occurring about the particle.

The same model can also be used to examine the overall structure of this microdiffusion flame. Figure 6 shows the radial profiles for temperature, oxygen, and methane. It is important to note that there was no provision for endothermic

devolatilization reactions. Rather the coal particle was allowed to float at the adjoining gas stream temperature. Results for two sizes of bituminous coal are shown on the figure, 40 and 80 microns.

Temperature overshoots for gas surrounding the coals (80 microns: 380K; 40 microns: 355 K) agree favorably with the results presented previously for the two color measurement of the burning coals [8]. The O_2 traces show that larger particles were significantly shielded from free stream O_2 . The deeper O_2 penetration for the 40 micron particle is due to the smaller total mass flow of volatile gases. The CH_4 profiles indicate a zone of about 1 mm diameter surrounding the 80 micron bituminous particles in which O_2 is depleted and CH_4 is present in excess of 1 percent. This region would have a large potential for soot formation, and indeed, the soot clouds previously observed for these particles are of this size [8]. Note further that the 40 micron particle exhibits considerably lower hydrocarbon levels. This is consistent with the earlier observation of no soot cloud accompanying these particles [8].

The observation of condensed material in the immediate vicinity of the coal particle suggests an alternate means of NO_x reduction. The reduction of NO by heterogeneous reaction is potentially important in both the immediate vicinity of the coal particle, and in the bulk fuel-rich zone. The importance of this means of reducing NO is the subject of the next section.

HETEROGENEOUS CHEMISTRY

The heterogeneous portion of this work was initially limited in scope to identifying the importance of heterogeneous NO reduction on soot relative to the overall NO reduction. The approach was to expose samples of gas containing NO to high temperature soot dispersions for short times in a single pulse shock tube. Details of the apparatus, procedure, and results are presented elsewhere [11]; only an outline of these are described here.

The single pulse shock tube is illustrated in Figure 7. The test section is isolated by the ball valve, drawn to a vacuum, and filled with the test mixture. At the same time the driven section is filled with inert gas. Prior to the shock the soot sample (carbon black; Cabot Corporation) is pneumatically dispersed into the test section. A laser extinction system is used to verify the pre-shock soot concentration. The ball valve is opened to allow communication between the driven and test sections, and the diaphragm is broken to initiate the test. Following the shock compression, the trailing rarification wave quenches the sample, which is withdrawn and analyzed for NO_x .

The results of a series of tests are shown in Figure 8, with the data reduced into Arrhenius form. The estimated uncertainty associated with the individual data points is shown for one datum. Early in the study the appearance of hydrocarbons in the shocked gas suggested that a homogeneous interference may be active. The tests were repeated with carbon black that had been thermally treated to remove these volatiles. These data showed no perceivable difference relative to the non-devolatilized material.

Figure 9 compares the rate derived here with rates obtained by others on chars, graphite, and carbon black. The key to the figure is contained in Table 1. The results suggest that the rate measured here is significantly faster than that measured for the other materials, with the exception of the two graphite measurements. A potential reason for the apparent higher rate is that a faster rate may manifest itself early in the reaction. After a few milliseconds of reaction the surface becomes chemically annealed and the global rate is reduced.

Indirect support for this came from Edwards [16] who stated that reduction of NO on graphitized carbon black appeared to be rapid at very short times.

GLOBAL COAL REACTION

The ultimate objective of the ongoing work is the evaluation of the relative contributions of homogeneous and heterogeneous kinetics to the reduction of nitrogen in coal flames. In order to have a basis for comparison, a comprehensive body of coal nitrogen reduction data under fuel-rich conditions has been developed in a tunnel furnace [17]. Work underway, but not reported here, includes:

- Development of global models of the nitrogen reduction behavior
- Data development on short time phenomena
- Data development on the coal reaction at the burnout point

Figure 10 illustrates a set of NO reduction data. Direct application of the gas-phase model, starting the reaction at the 0.3 sec point, yields the behavior indicated by the dashed line. The data set of Figure 11 illustrates NO decay from another similar experiment. Here, the heterogeneous reaction rate indicated in Figure 8 is applied to the data. The soot concentration in the coal experiment is the only variable. If 5 percent of the ASTM volatile matter is converted to soot, the decay in NO can be fully accounted in terms of heterogeneous reaction.

At the present stage, neither homogeneous or heterogeneous reactions can be eliminated as important means of removing NO_x in the fuel-rich zone of the reburning or staged combustion process. The key uncertainty is the amount of soot present during the fuel-rich process. Continuing work is directed toward resolving these issues.

CONCLUSIONS

The research reported here has led to the development of a homogeneous reaction kinetics model for the processes governing fuel-nitrogen reactions in coal flames. The exercising of the model against staged combustion and reburning data have tentatively identified the steps controlling the destruction of fixed nitrogen. The development of a data base on the heterogeneous reaction of NO on a soot surface has led to the development of kinetic expressions for this step. Comparison of homogeneous and heterogeneous NO reduction rates for fuel-rich coal combustion conditions does not presently justify the exclusion of either step.

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TABLE 1. SELECTED RATE CONSTANTS FOR NO REDUCTION
ON VARIOUS CARBONACEOUS MATERIAL

FIGURE 9 CURVE	MATERIAL	RATE CONSTANT, K (moles $\text{s}^{-1}\text{m}^{-2}\text{atm}^{-1}$)	REFERENCE
A	carbon black	$4.5 \times 10^1 \exp \left[\frac{-19176}{RT} \right]$	present study
B	Montana lignite char	$2.3 \times 10^2 \exp \left[\frac{-35050}{RT} \right]$	[12]
C	Montana lignite char	$5.0 \times 10^1 \exp \left[\frac{-32590}{RT} \right]$	[13]
D	graphite	$1.0 \times 10^6 \exp \left[\frac{-49680}{RT} \right]$	[14]
E	graphite	$2.9 \times 10^6 \exp \left[\frac{-58030}{RT} \right]$	[15]
F	Utah bituminous char	$2.4 \times 10^1 \exp \left[\frac{-24240}{RT} \right]$	[15]
G	Pennsylvania anthracite char	$2.2 \times 10^1 \exp \left[\frac{-24240}{RT} \right]$	[15]
H	graphitized carbon black	$4.3 \times 10^4 \exp \left[\frac{-14310}{RT} \right]$	[16]

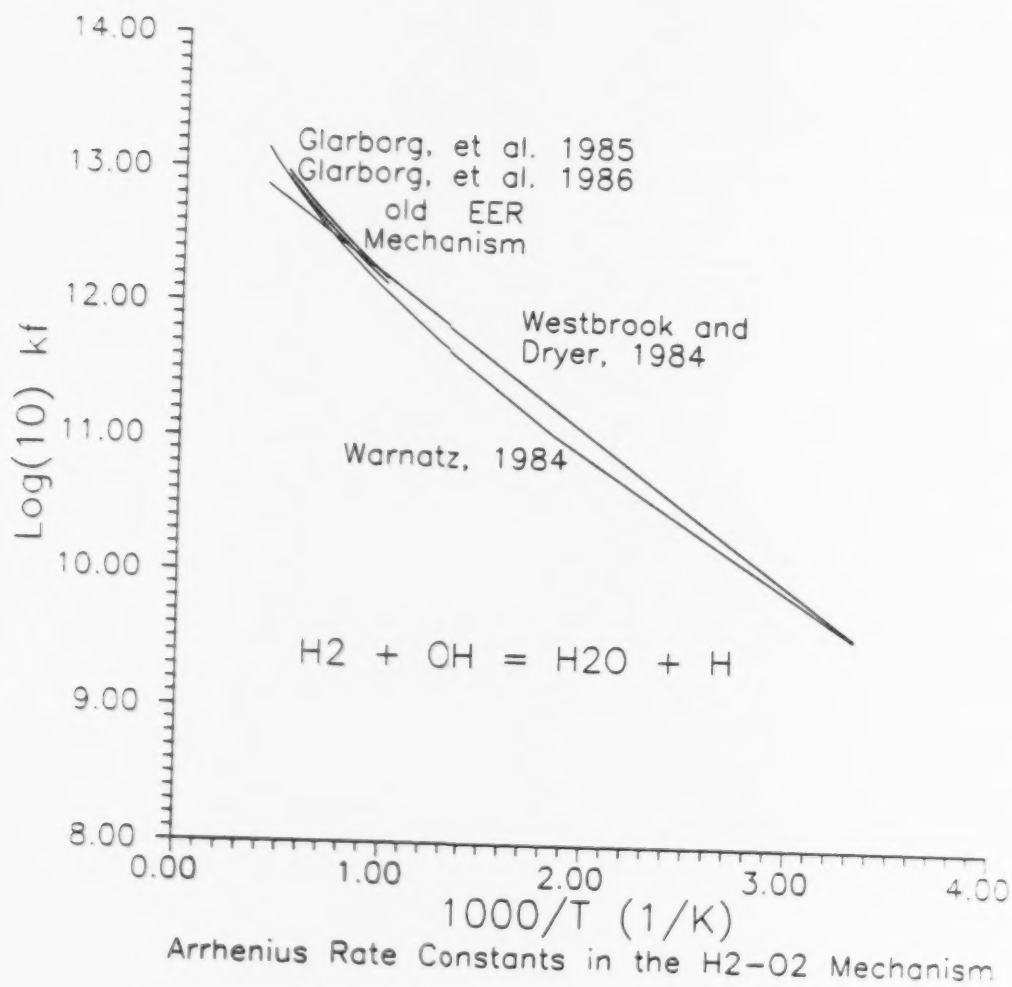


Figure 1. Comparison of rate constants for the reaction of hydrogen with hydroxyl radical.

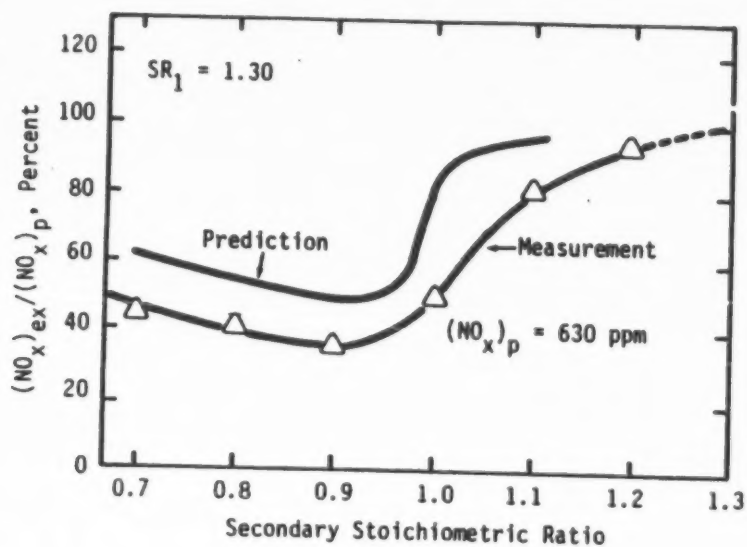


Figure 2. Comparison of bench-scale reburning data against the homogeneous model.

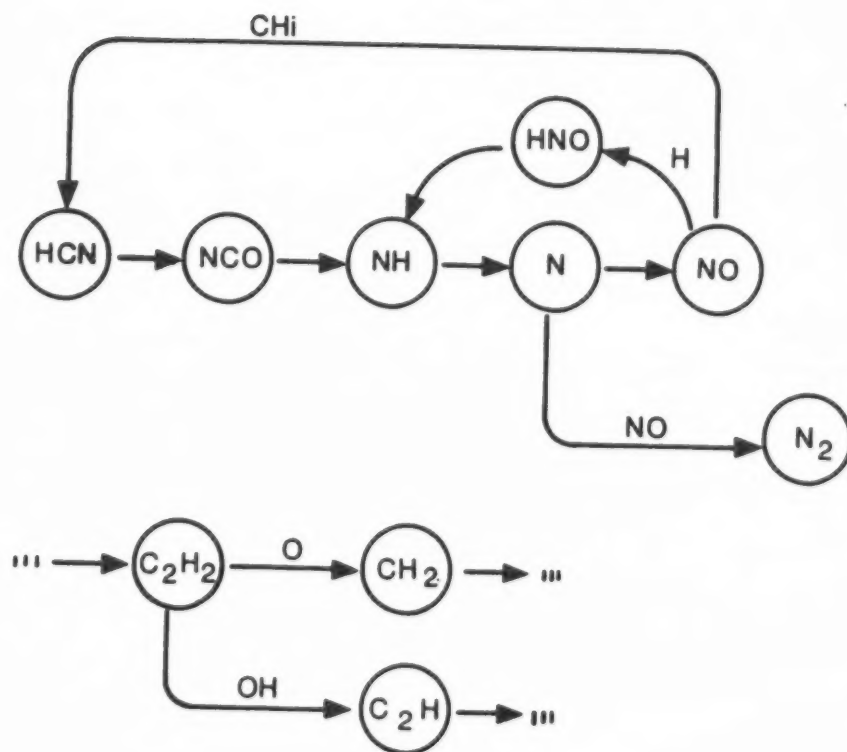


Figure 3. Nitrogen reduction pathways opened by the reburning process.

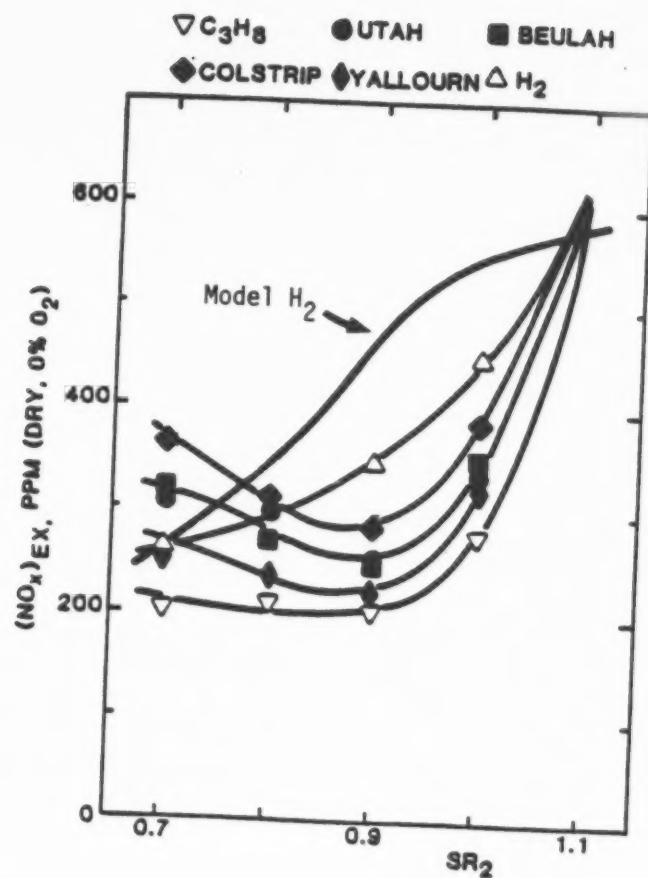


Figure 4. The influence of fuel type on reburning effectiveness.

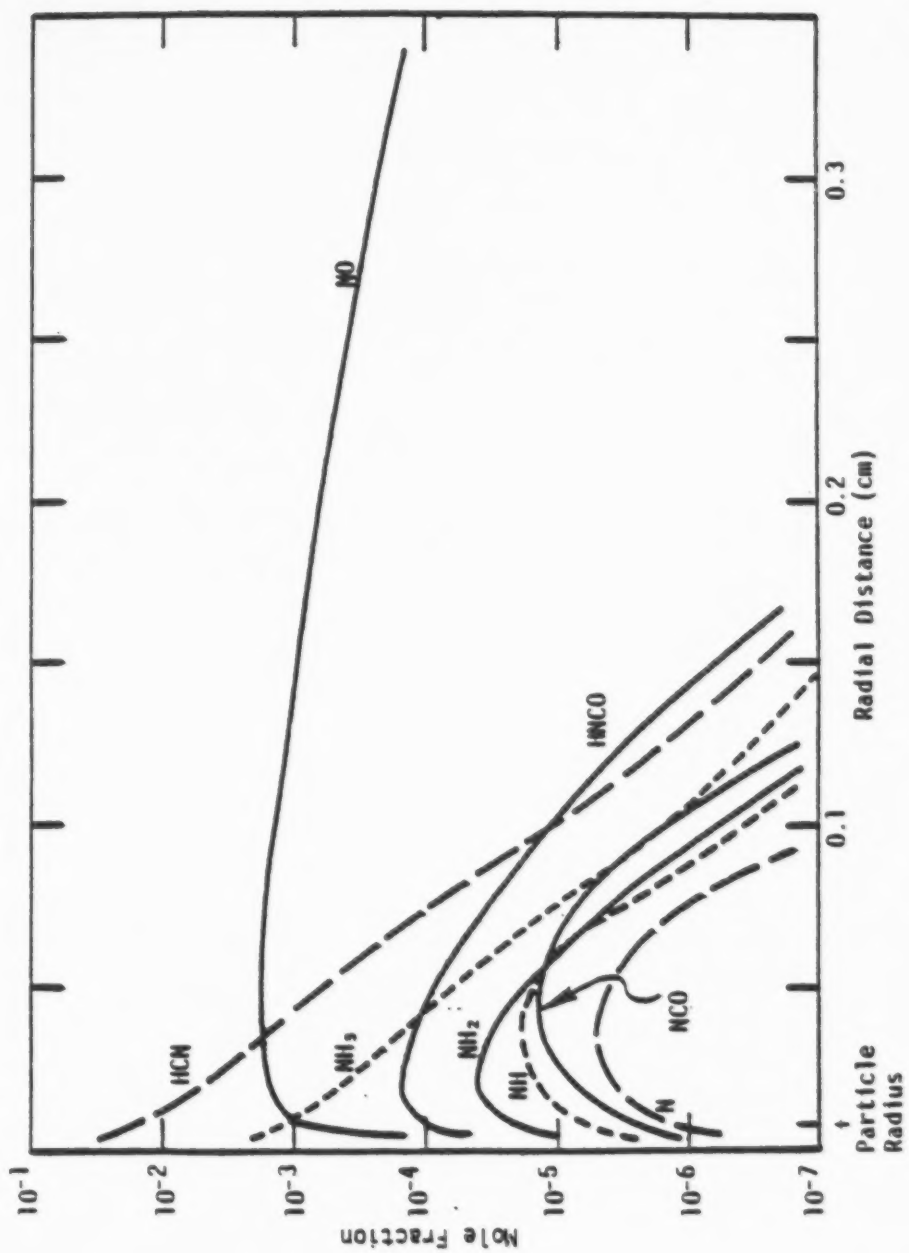


Figure 5. Calculated nitrogen species profiles in the vicinity of a devolatilizing coal particle.

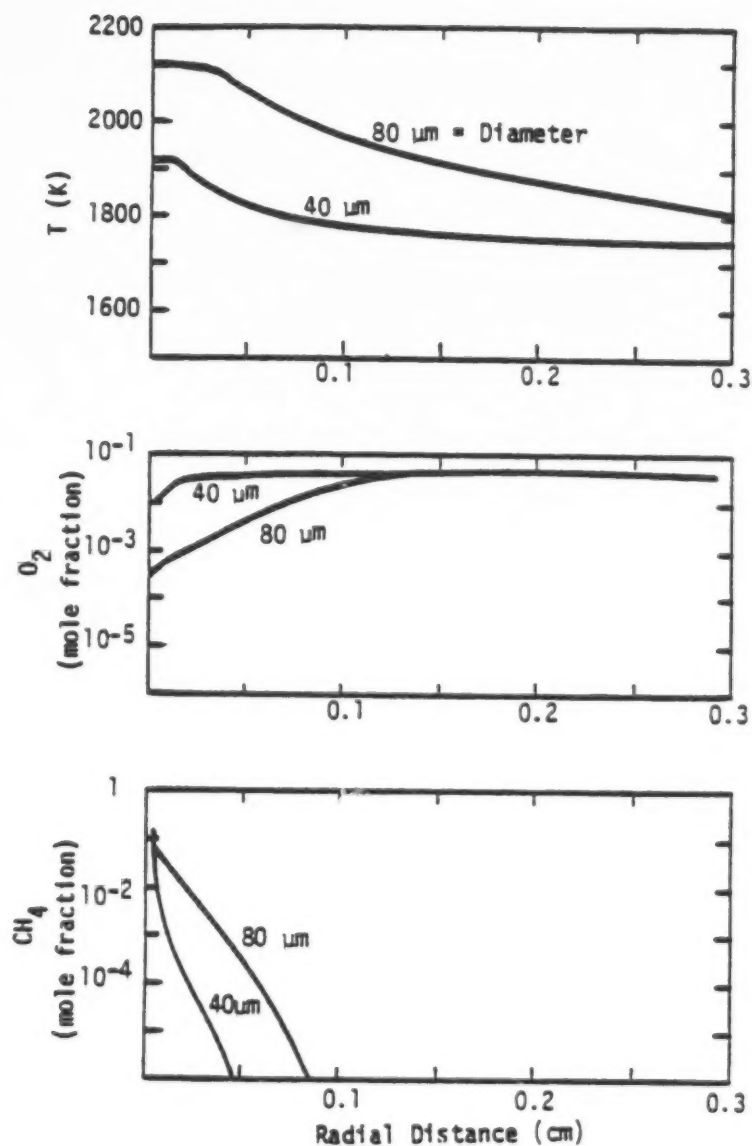


Figure 6. Influence of particle size on the temperature, oxygen, and methane fields about a devolatilizing coal particle.

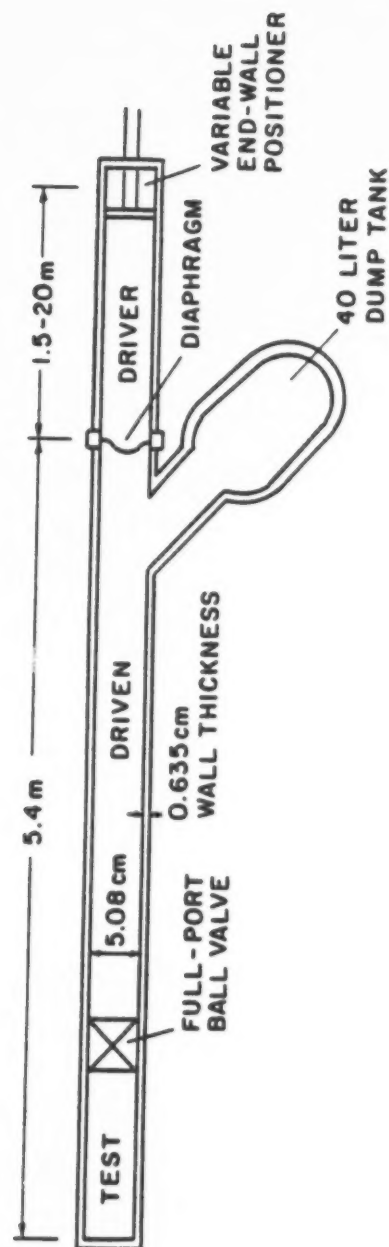


Figure 7. A general schematic of the single-pulse shock tube.

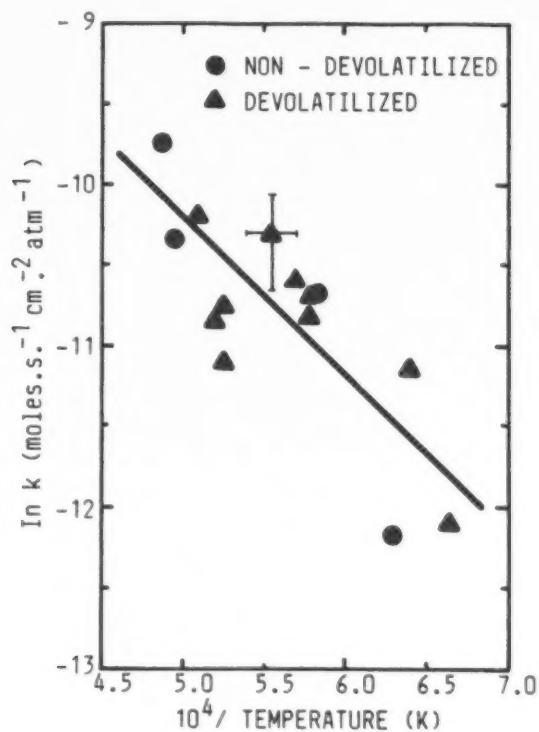


Figure 8. Reduced kinetic rate of NO destruction on dispersed soot.

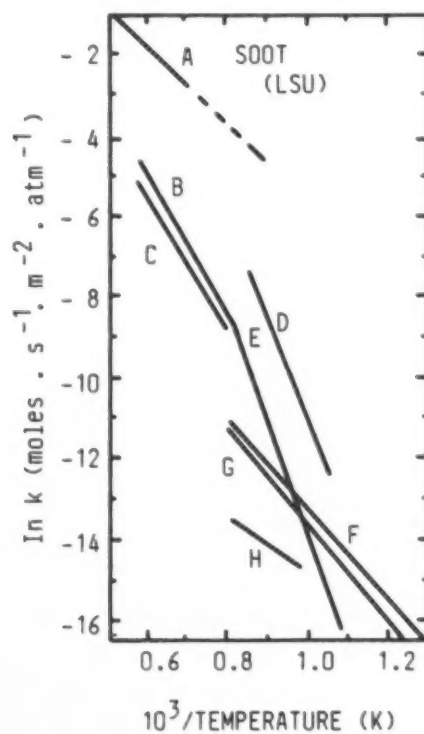


Figure 9. Comparison of current rate with that generated in other studies (key is in Table 1).

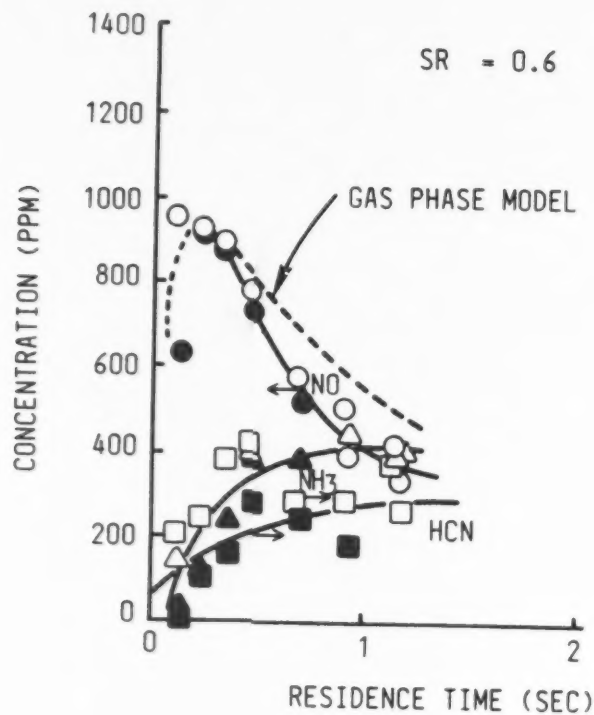


Figure 10. Comparison of NO reduction in a fuel-rich pulverized coal flame with homogeneous modeling.

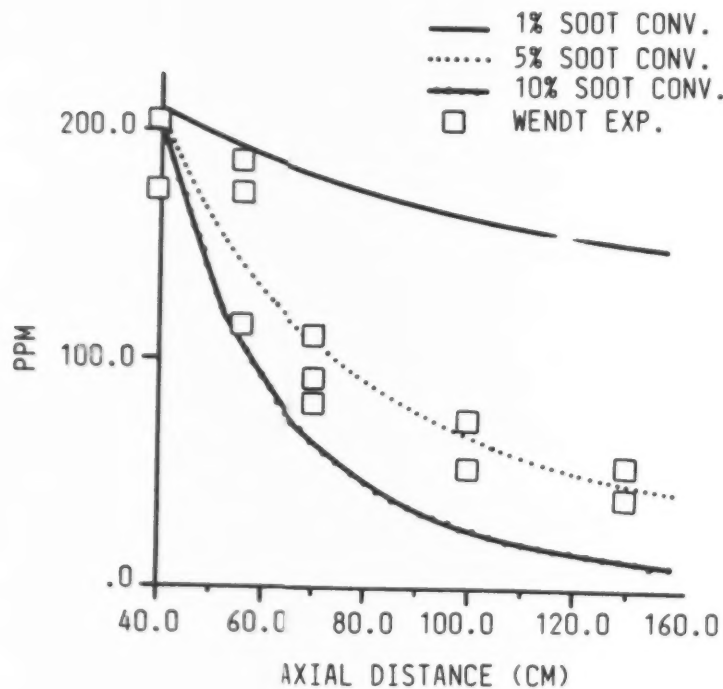


Figure 11. Comparison of NO reduction in a fuel-rich pulverized coal flame with heterogeneous modeling.

THE INTERPLAY BETWEEN CHEMISTRY AND FLUID MECHANICS IN THE
OXIDATION OF FUEL NITROGEN FROM PULVERIZED COAL

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ABSTRACT

The evolution and subsequent reaction of gas-phase nitrogenous species from pulverized Montana Rosebud sub-bituminous coal have been measured in the Stanford entrained-flow reactor under uniform and well controlled conditions. Experiments have been performed at atmospheric pressure with temperatures up to 1850K and oxygen concentrations varying from zero to 15.0%. Gas-phase measurements have been made of carbon oxides, light hydrocarbons, NO, NO₂, N₂O, NH₃, and HCN. Chemical and physical analyses of partly reacted coal particles provide data on the carbon and nitrogen content, porosity, and the rate of tar pyrolysis. A major focus of this research has been the role of tar in the evolution of fuel nitrogen. At high heating rates it is found that substantial quantities of tar are evolved in very short reaction times and that the pyrolysis products are rich in nitrogen. The rate of reaction of these products in and around a volatile cloud surrounding the parent coal particle controls the oxidation of fuel nitrogen. The measurements show that when the pyrolyzing coal particles are exposed to oxygen concentrations as low as 4% a significant portion of the fuel nitrogen can be oxidized to NO, although some of this NO is subsequently reduced in the gas phase.

INTRODUCTION

During the early stages of pulverized coal combustion a coal particle experiences rapid heating, and pyrolysis occurs concurrently with the oxidation of combustible pyrolysis products. The Stanford entrained-flow reactor has been designed to study this phenomenon, under uniform and well controlled conditions. A wide range of oxygen concentrations, particle sizes, and gas temperatures has been studied, with all these parameters independently controlled. Previous work at Stanford (1,2) has documented a rapid release of material from coal particles at high heating rates (typically 10^4 K/sec). This material is not immediately observed as gas-phase species, and under certain conditions the delay between the ejection of material and its conversion to gas-phase species can become quite significant. This phenomenon is thought to result from the formation of a volatile cloud surrounding individual particles, whereby pyrolysis products oxidize around the parent particle. This has been observed in the Stanford reactor (3), and a number of other researchers have hypothesized or observed the formation of a volatile cloud (4,5,6,7). Of particular interest is the role that tar plays in the volatile cloud, as tar has been found to contain nitrogen in concentrations similar to the parent coal, for a wide variety of coal types (8,9). Results with Montana Rosebud sub-bituminous coal at Stanford have indicated an enhancement of the tar nitrogen yield over the parent coal. The fate of the volatile cloud (and hence much of the fuel nitrogen) has strong implications as to the overall question of NO_x formation during pulverized coal combustion.

EXPERIMENTAL PROCEDURES

EXPERIMENTAL FACILITY

The Stanford entrained-flow reactor is designed to provide a well-controlled high temperature environment in which to study the reactivity of pulverized coal. A high temperature gas is generated with an argon arc-jet and the subsequent dilution with a combination of argon, nitrogen, and oxygen (Figure 1). To study fuel nitrogen conversion, no N_2 is added to the gas flow. Independent control of the bulk gas temperature and oxygen concentration is possible, with gas temperatures ranging from 1150K to 2000K, and oxygen concentrations ranging from 0.0% to 15.0%. This hot gas flows through a test section which is surrounded by an insulated guard heater, allowing nearly constant gas temperatures. The test section consists of a 5.88 cm diameter tube lined with refractory brick. Gas velocities in the test section range from 3 to 5 m/sec, which results in particle residence times from 0 to 150 msec. The test section has four optical access ports which, along with axial movement of the coal injector, allows for the observation of coal particle luminosities over nearly the entire range of residence times. A dilute suspension of pulverized coal is introduced along the centerline of the test section at a nominal mass flow rate of 2 grams/min, supplied by a fluidized bed feeder. This feed rate insures a low particle loading in the reactor (less than 10 particles/cc), and hence single particle combustion. Gas and particle samples are collected through a single probe which can be traversed to any location in the reactor.

After injection into a high temperature environment, coal particles are rapidly heated through conduction from the bulk gas, augmented by radiation from the reactor wall. Coal particles are rapidly mixed into the gas stream, and very quickly follow the direction of mean gas flow. Streak photographs taken with a high speed movie camera show that the particle/gas slip velocities are very low. This allows for a determination of the particle residence time from the bulk gas velocity and the distance traveled after injection. The gas-phase pyrolysis/combustion products are collected by drawing them into a cooled sample line with a vacuum pump. Rapid cooling of the gas through conduction to the probe quenches chemical reactions quickly. This gas stream is then passed through a number of different instruments to determine its chemical composition. Particle samples are collected by drawing the hot gas/particle stream into the probe through a quenching water spray. The resulting water/particle mixture is collected, and the solids are later extracted for analysis.

DIAGNOSTICS

Gas-Phase Sampling

Gas samples collected through the sampling probe are analyzed for a number of different chemical species. The main diagnostic used to determine the extent of coal oxidation is the percent conversion of carbon into gaseous species. CO and CO₂ levels are measured with non-dispersive infrared analyzers, and a gas chromatograph is used to determine the concentrations of light hydrocarbons (up to the C₄ group). The oxygen concentration in the reactor is monitored with an electrochemical analyzer. The measurement of gas-phase nitrogenous species is performed through a number of techniques. A chemiluminescence analyzer measures both NO and NO₂ concentrations, while N₂O is measured with the gas chromatograph. HCN and NH₃ concentrations are determined through the absorption of these species in solutions, and the measurement of their molar concentrations with ion-specific electrodes.

The percent conversion of carbon and nitrogen in the feed coal into gas-phase species is determined by a mass-flux balance technique. The fluidized bed feeder supplying the coal particles to the coal injector is suspended from a Mettler electronic balance, and the weight is monitored throughout each experimental run. The feedrate is very stable, with a maximum fluctuation over a period of 30 minutes of less than 5 percent. The percent by mass of both carbon and nitrogen in the raw coal has been determined by an ultimate analysis of the coal, which has been performed by an outside laboratory. Thus the molar flux of carbon and nitrogen input to the reactor is a known quantity. The flux of carbon or nitrogen as any particular chemical species in the gas phase is determined through the measurement of radial concentration profiles in the reactor, and integrating the concentration multiplied by the well characterized velocity profile. The resulting gas-phase molar flux is then divided by the input flux to the reactor, resulting in the percent conversion to a particular gas-phase species. It is important to note that this technique does not account for material which is ejected from the coal particles, but has not been converted to gas-phase species. The observation of a delay between pyrolysis observed through analysis of particle samples and the ultimate conversion of pyrolyzed material (especially tars) into gas-phase species has motivated much of the work described in this paper.

Partly-Reacted Particles

The collection of partly-reacted coal particles and condensable pyrolysis products (tars) allows a number of analytical procedures to be performed. Useful qualitative information is gathered through the use of scanning electron microscopy (SEM). Samples of partly-reacted particles are prepared for study through gold-palladium sputtering. The surface morphology of the particles can be examined in some detail, and the presence or absence of "tarry volatiles" (here defined as condensable species and tars) can be noted. The presence of tarry volatiles is characterized by an amorphous structure which is built up from individual elements with a typical dimension of several microns. The tarry volatiles are thought to represent material ejected from the coal particles during pyrolysis, leaving large internal voids. Since the coal used in this study is a non-swelling coal, the bulk density of dried samples is related to the extent of mass loss. Particles become more and more porous as mass is ejected during pyrolysis. Sufficient quantities of partly-reacted particles (typically 10 cc) are collected to allow a determination of the sample bulk density. The dried sample is placed in a graduated cylinder, and compacted with a strong mechanical vibration. The sample volume is read, and the sample is weighed, giving a bulk density.

To quantify the internal porosity of partly-reacted particles, it is necessary to examine the internal structure of individual coal particles. This is done through the use of cross-section micrography. A coal sample is mixed into an epoxy resin, which is allowed to harden under pressure to form a briquette. This hardened sample is then polished, exposing cross-sections of individual particles. A light microscope is then sufficient to examine the internal macro-structure. To quantify the internal void area observed, an image processing technique has been developed. A photograph of the cross-section is digitized into a 512x512 array, which is then processed to determine the ratio of the internal void area to the total

exposed surface area. This internal void area represents the large voids only, with the resolution of the digitizing system at about 0.2 microns. There is a substantial particle to particle variation in the "apparent porosity" measured by this technique, so a statistical sample must be analyzed to determine the apparent porosity for each experimental condition.

One final analysis performed is the determination of the carbon, hydrogen, nitrogen and ash content of small (2-3 mg) samples. This is performed by an outside laboratory, using a Control Equipment Corporation model 240-X analyzer. The C,H,N, and ash analysis is performed through the combustion of an accurately weighed sample in pure oxygen under static conditions. This provides a useful back-up to the gas-phase species measurements, as well as providing valuable information concerning the fate of fuel nitrogen during devolatilization.

EXPERIMENTAL RESULTS

GAS PHASE CONVERSION

The main diagnostic following the extent of coal oxidation in the Stanford flow-tube reactor is the conversion of carbon into gas-phase species. This has been measured under a range of gas temperatures from 1150K to 1750K, and oxygen concentrations from 0 to 15%. Figure 2 shows a summary of data obtained for narrowly size-graded Montana Rosebud subbituminous coal, with a nominal diameter of 55 microns. The important feature to note in Figure 2 is the strong dependence of the rate of carbon conversion on the oxygen concentration. The effect of the bulk gas temperature is quite strong as well, with increasing coal reactivity at higher temperatures. These results are reproducible from experiment to experiment with a typical variation of plus or minus five percent.

The low particle loading in the Stanford reactor is used to insure negligible particle-particle interactions. Thus the oxygen concentration under stoichiometric conditions would be quite low, at about 0.5%. The bulk of the experiments performed to date have been at oxygen concentrations ranging from 2.0% to 7.6%, where the majority of coal nitrogen has been observed to be rapidly converted to NO. Under these conditions there is a strong correlation between the conversion of carbon to gas-phase species (primarily CO₂) and the conversion of fuel nitrogen to NO. Figure 3 shows the percent conversion of carbon and nitrogen plotted against residence time, at a temperature of 1350K and an oxygen concentration of 4.0%. The conversion of fuel nitrogen to NO follows the carbon conversion up to a level of about 70%, where the nitrogen conversion reaches an asymptote. Figure 4 compares the conversion of fuel nitrogen to NO with the carbon conversion for three experimental conditions, as listed in the figure. All show an ultimate conversion of fuel nitrogen to NO of about 70-80%.

One interesting feature observed in the NO conversion measurements is seen in Figure 5. For a fixed oxygen concentration, the ultimate formation of NO appears to be independent of (or at least insensitive to) the gas temperature. This observation has been made by other researchers (10,11). One other important feature seen in Figure 5 is the reduction of NO seen at an early stage of combustion. Reaching a maximum level of about 86% conversion to NO, this value then drops to a value of about 70%, thus indicating the existence and importance of gas-phase NO removal mechanisms under these conditions.

Recent tests performed with no oxygen added to the reactor have shown very low conversion rates of fuel nitrogen to NO. Figure 6 shows the conversion to NO as a function of oxygen concentration, at a gas temperature of 1350K. With no oxygen added, there is only a very low level of NO detected in the reactor. Measurements of NH₃ and HCN under this condition have shown low levels as well, with approximately twice as much HCN as NO, and slightly less NH₃ than NO. The total conversion of fuel nitrogen to NO, HCN and NH₃ observed under these conditions is approximately 10%. This is consistent with results obtained at this temperature by Freihaut, et al. (8), and Solomon and Colket (9), using a heated grid apparatus to study coal nitrogen release during devolatilization.

PARTLY-REACTED PARTICLES

The collection of partly-reacted particles and condensible pyrolysis products (tars) is a valuable aid in interpreting the gas-phase conversion results. Figure 7 shows an S.E.M. of a sample collected at a residence time of 10 msec and a temperature of 1750K, in an inert environment. In addition to the partly-reacted coal particles collected, which are the same size as the raw coal, an amorphous "tarry structure" is observed. A significant quantity of condensed tars is collected only under low oxygen conditions. The appearance of these tarry structures occurs at a very early time in the reactor, with the extent of tar release apparently completed by the earliest time particle samples can be collected. For the conditions of Figure 7, this represents a residence time of only 10 msec.

To quantify the early tar release observed in the Stanford reactor, cross-section micrographs have been used. Figure 8 shows the internal structure of a particle collected at a residence time of 10 msec, at a gas temperature of 1750K. The large internal voids appear uniformly throughout the particle cross-section, and make up a significant fraction of the total cross-sectional area. The ratio of the void area to the exposed surface area is thought to represent the percent mass ejected, primarily as tar. Quantitative determination of this relative void area as a function of residence time and oxygen concentration has been performed using a digitizing and image-processing system, with the results shown in Figure 9. The apparent porosity of partly-reacted particles jumps to a level near 60% very rapidly. Sampling at times earlier than 10 msec are not possible due to design restrictions of the sampling probe. The curves shown represent a gas temperature of 1750K, and oxygen concentrations of 0.0% and 7.6%, respectively. A rapid ejection of material is detected, followed by a relatively gradual increase in the internal void area. In general, the apparent porosity of particles exposed to an oxidizing environment is only slightly higher than those from an inert environment.

To verify the apparent porosity results, bulk density measurements have been performed on partly-reacted particles. The measured bulk densities of dried particle samples may not accurately represent the behavior of the parent particles themselves, due to the possible collection of condensible pyrolysis products along with the particles. However, bulk density measurements would be expected to follow the same trends observed in the apparent porosity. Figure 10 represents the bulk densities of particle samples collected at a gas temperature equal to that in Figure 9. The same qualitative trend is observed, with a rapid decrease in the bulk density occurring in less than 10 msec, and a relatively gradual decrease thereafter. The bulk density results are also relatively insensitive to the bulk gas oxygen concentration.

Partly-reacted particle samples have been analyzed to determine their carbon, hydrogen, nitrogen, and ash content. It is not currently possible to separate the tar evolved during pyrolysis from particle samples, so to date analysis has only been performed for particles exposed to an oxidizing environment. Under such conditions, little if any tar is observed in the samples collected. The resulting elemental composition of the partly-reacted particles is listed in Table 1. The particle carbon percentage increases as volatile species are evolved, and the hydrogen content drops rapidly. The nitrogen content appears to drop very rapidly, reaching a value of about one-third of its initial value by a residence time of 20 msec. This indicates that the char product is nitrogen poor, and the tar evolved is nitrogen rich.

DISCUSSION

MODEL MOTIVATION

The discrepancy between the particle mass loss determined through cross-section micrographs and the gas-phase conversion rates measured has led to the development of a simple model for the oxidation of tarry volatiles. In this model the conversion of carbon to combustion products at early times is considered to arise from two sources. The first is the combustion products observed in an inert environment, which represents about 25% of the original coal carbon. This occurs rapidly, and is nearly complete at a time of 10 msec. The oxygen present in the feed coal is accounted for in the CO and CO₂

evolved in an inert environment. The second source is represented by the diffusion-limited combustion of a cloud of pyrolysis products surrounding the parent coal particle. This cloud is considered to form during the first 10 msec after introduction into the high temperature environment, with no source from the parent coal particle thereafter. It then oxidizes as a shrinking sphere until the flame sheet reaches the particle surface. The amount of material in this cloud is determined from the apparent porosity measurements. The fraction of the original coal carbon contained in this cloud is estimated to be 45%.

The initial diameter of the volatile cloud, required for this model, is taken from visual observations of individual luminous sources in the Stanford reactor. These observations have been made using a magnification lens train and a high speed movie camera. The observed diameters of these volatile clouds range from 3 to 5 times larger than the original coal particle. These limits have been used as bounds for the model calculations. This model does not attempt to directly represent the history of mass ejection during heat-up, or the oxidation which occurs during the first 10 msec. The initial conditions used are those determined experimentally at a residence time of 10 msec (the earliest time that particle samples can be collected to determine the amount of tar released). The purpose of this calculation is to estimate whether the mechanism of diffusion-limited combustion of tarry volatiles in a volatile cloud surrounding the parent particles can account for the substantial delay observed between mass ejection and subsequent oxidation to gas-phase species.

MODEL DEVELOPMENT

The rate of change of material in the volatile cloud surrounding an individual coal particle is determined by the rate of oxygen diffusion to the surface of the volatile cloud. It is assumed that the combustion of the tarry volatiles is fast, and that as a result the combustion rate is limited by the transport of oxygen to the cloud. Under these conditions, the balance between oxygen transport to the cloud and the rate of change of the size of the cloud is seen in Eqn 1:

$$\frac{d}{dt} \left[\frac{4\pi}{3} (r_c^3 - r_p^3) \rho_v \right] = -K4\pi r_c \quad (1)$$

where:

r_c = radius of the volatile cloud.

r_p = radius of the coal particle.

ρ_v = density of the tarry volatiles.

K = factor representing diffusion of oxygen to the cloud.

$$K = \frac{aT^{3/4} P_{O_2}}{\rho_v}$$

and:

a = a constant.

T = Temperature, deg K.

P_{O_2} = partial pressure of oxygen in the bulk gas.

Equation 1 can be integrated, and initial conditions applied, to set up the basic equation of the diffusion-limited model. The amount of carbon converted to gas-phase species has been normalized, with the resulting equation representing the percent conversion of coal carbon into gas-phase species, as given in Equation 2:

$$\chi = \chi_o + \frac{\chi_e - \chi_o}{(1 - r_p^3/r_o^3)} \left[1 - \left(1 - \frac{Kt}{r_o^2} \right)^{3/2} \right] \quad (2)$$

The parameters of this equation are listed below.

- χ = the percent carbon converted to gas-phase species.
- χ_o = the percent carbon converted to gas-phase species in an inert environment.
- χ_e = the total percentage of carbon converted just after exhaustion of the volatile cloud.
- r_o = the initial radius of the volatile cloud.

The calculations performed with this simple model are presented in Figure 11. In general, the results show trends similar to those observed in the Stanford flow-tube reactor. The bounds for each oxygen concentration case represent the limits of the initial volatile cloud size at three to five times that of the coal particle. The overall agreement between this model and the trends measured experimentally indicate that diffusion-limited oxidation of a cloud of tarry volatiles surrounding individual coal particles may represent the mechanism by which the ejected tars are oxidized. This will have important implications as to the fate of the nitrogen released along with the tar.

CONCLUSIONS

Substantial conversion rates of fuel nitrogen to NO have been observed at oxygen concentrations as low as 4.0%. At temperatures ranging from 1350K to 1850K, the ultimate conversion of fuel nitrogen to NO appears to be independent of the bulk gas temperature, and strongly dependent on the oxygen concentration. Substantial conversion of fuel nitrogen to NO is even noted at an oxygen concentration of only 0.4%.

The rapid pyrolysis of substantial quantities of material from coal particles under pulverized coal combustion conditions, along with the enhanced nitrogen content of this material, indicates that the mechanism by which pyrolysis products oxidize is of fundamental importance in understanding the conversion of fuel nitrogen. A time-lag between pyrolysis and the appearance of combustion products has been observed, with the rate of conversion of pyrolyzed material to gas-phase species a strong function of the oxygen concentration. The observation of individual luminous sources, and hence the existence of a reacting volatile cloud, has led to the development of a model representing combustion occurring in an unsteady shrinking sphere surrounding individual coal particles. This model shows reasonable agreement with the gas-phase conversion rates measured in the Stanford reactor, indicating that this mechanism may represent the conditions under which a substantial portion of the fuel nitrogen is oxidized.

The mechanism of tar oxidation as an unsteady shrinking sphere indicates that the conversion of fuel nitrogen contained in the tar would be dependent on the stability of the volatile cloud. The volatile clouds observed have diameters from 3 to 5 times that of the parent coal particles, and are thus large

enough to be influenced by the flow conditions around them. In particular, there are implications as to the interplay between fluid mechanics and the conversion of fuel nitrogen through the role that small scale turbulence might play in the disruption of the volatile clouds.

ACKNOWLEDGEMENT

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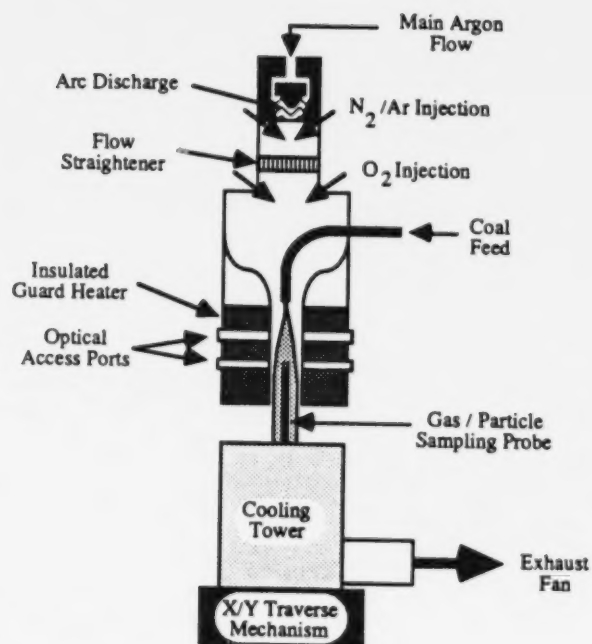


Figure 1. Entrained-flow reactor.

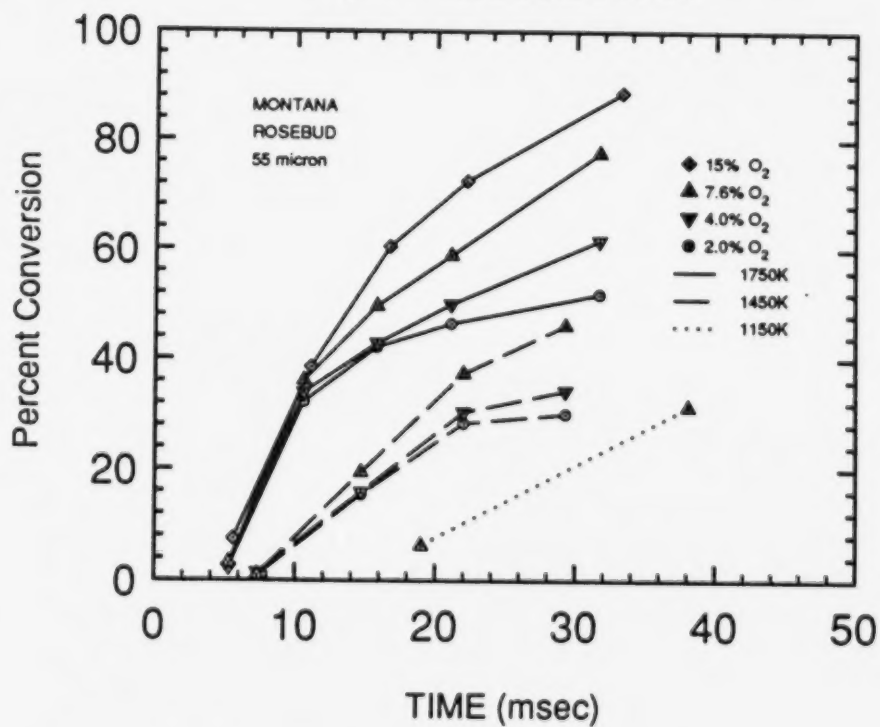


Figure 2. Carbon conversion results.

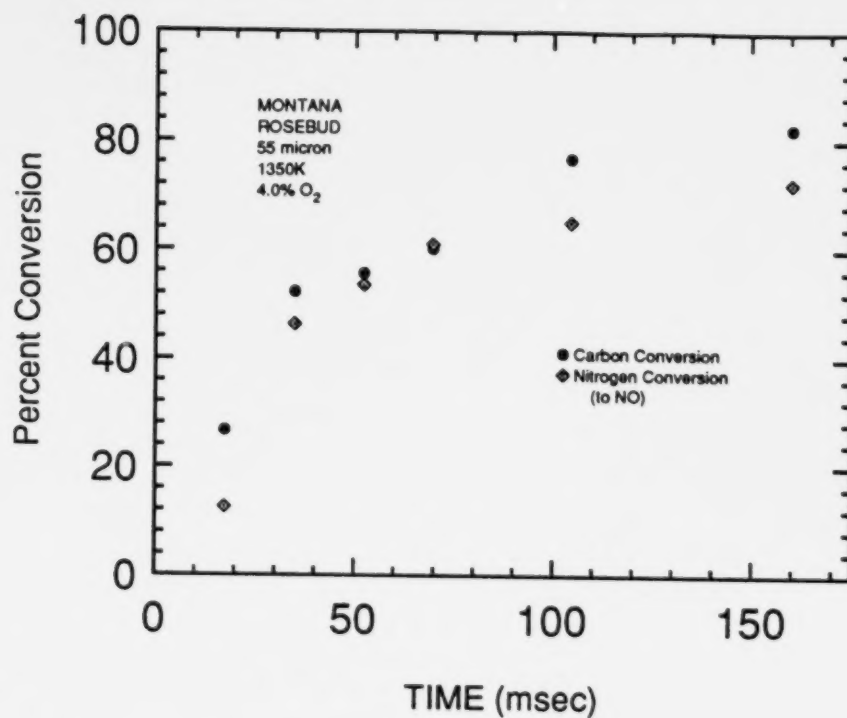


Figure 3. Carbon vs. nitrogen conversion.

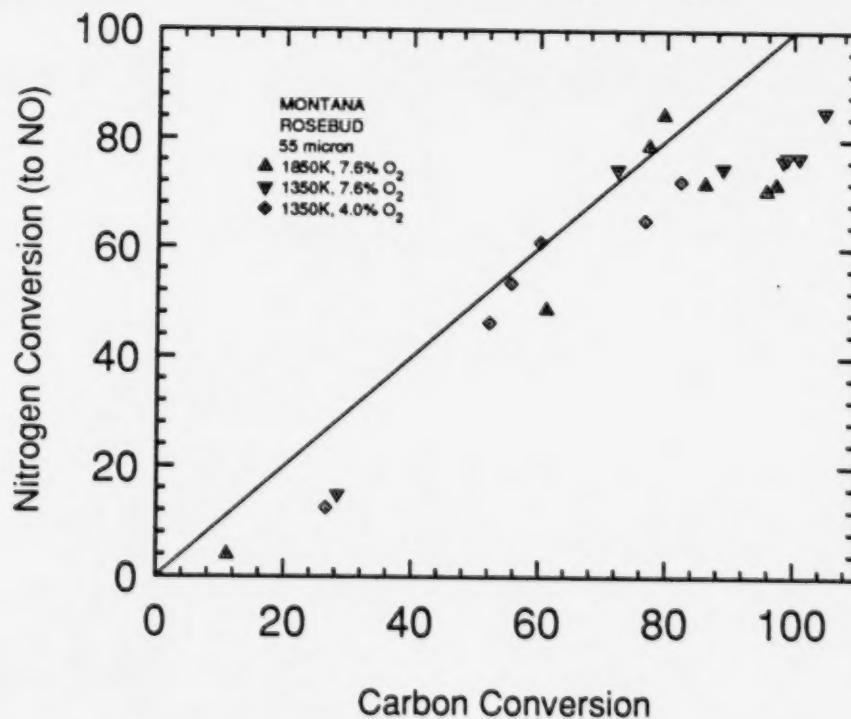


Figure 4. Fuel nitrogen conversion to NO.

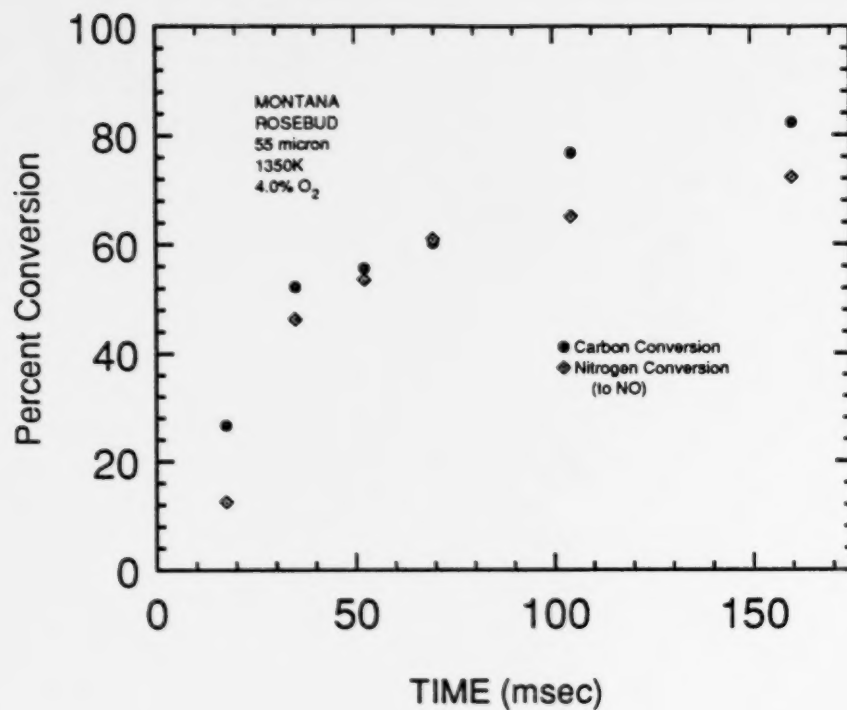


Figure 3. Carbon vs. nitrogen conversion.

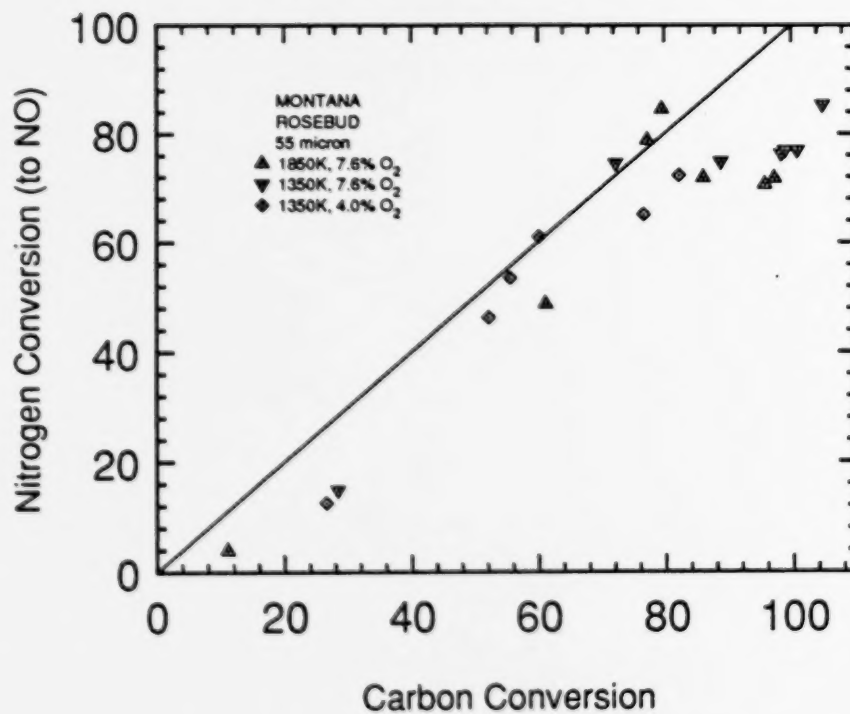


Figure 4. Fuel nitrogen conversion to NO.

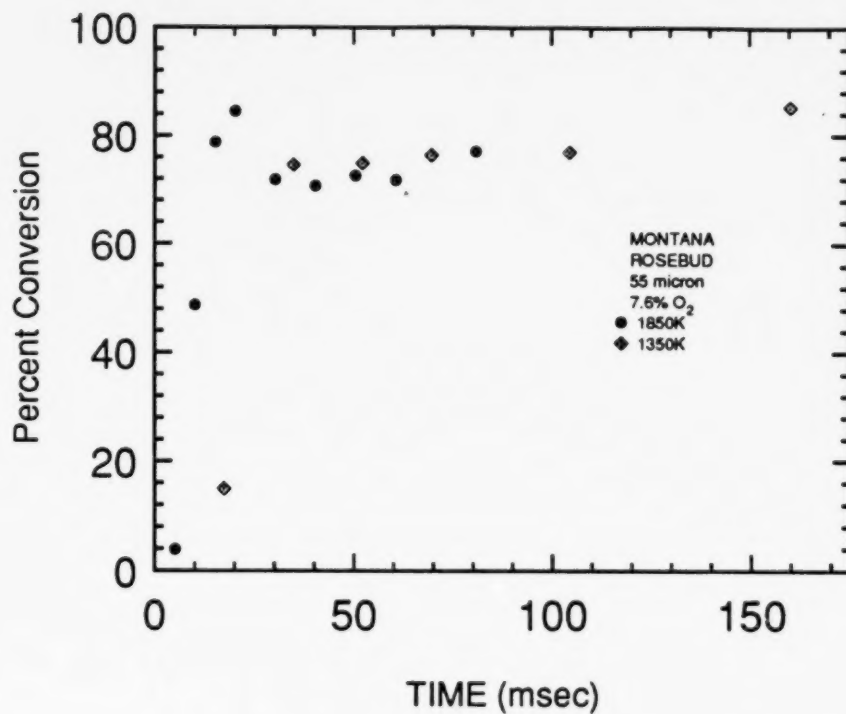


Figure 5. Fuel NO conversion dependence on gas temperature.

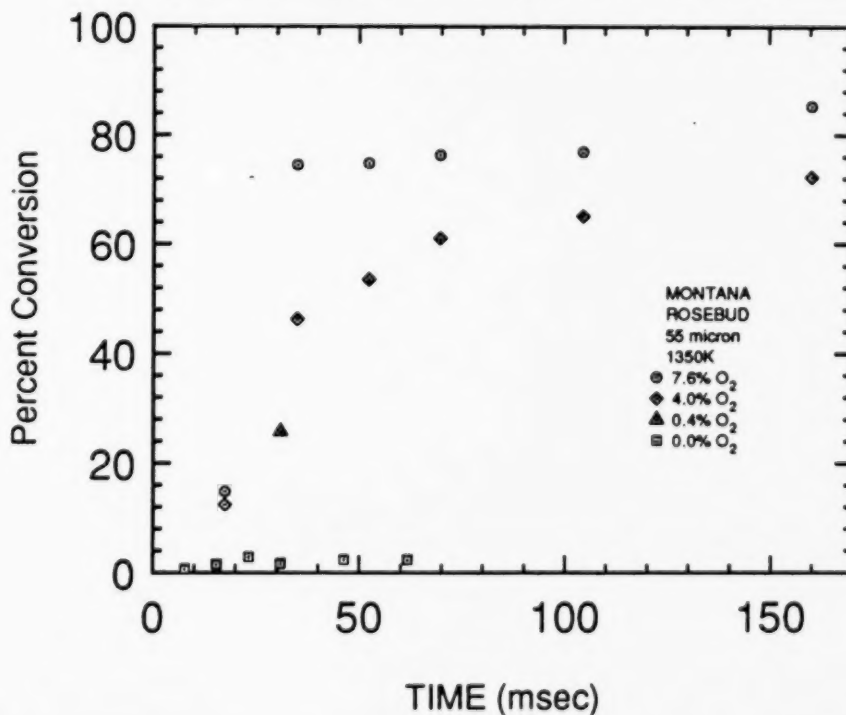


Figure 6. Fuel nitrogen conversion dependence on O₂ concentration.

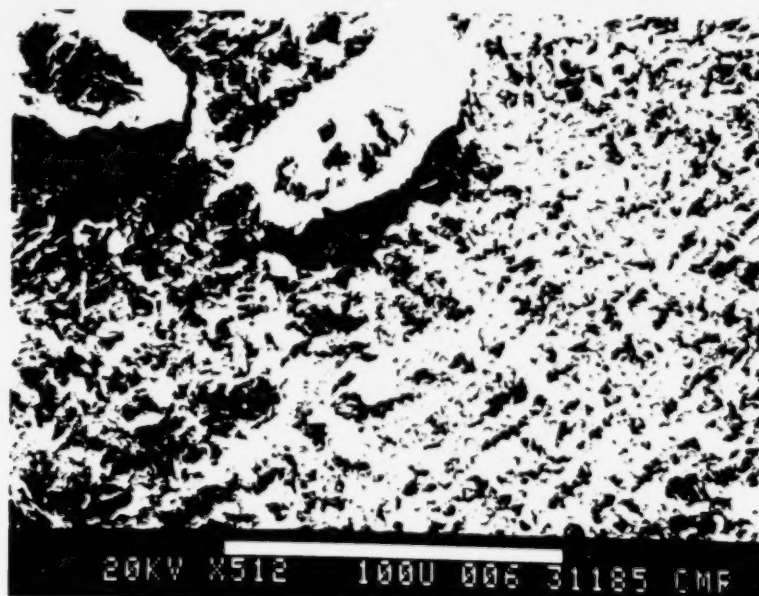


Figure 7. Scanning electron micrograph : 1750K, 10 msec.

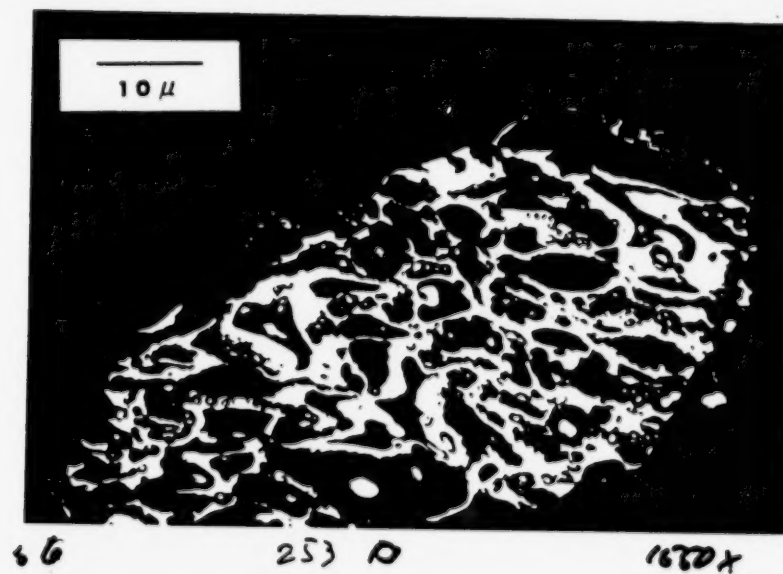


Figure 8. Cross-section micrograph : 1750K, 10msec.

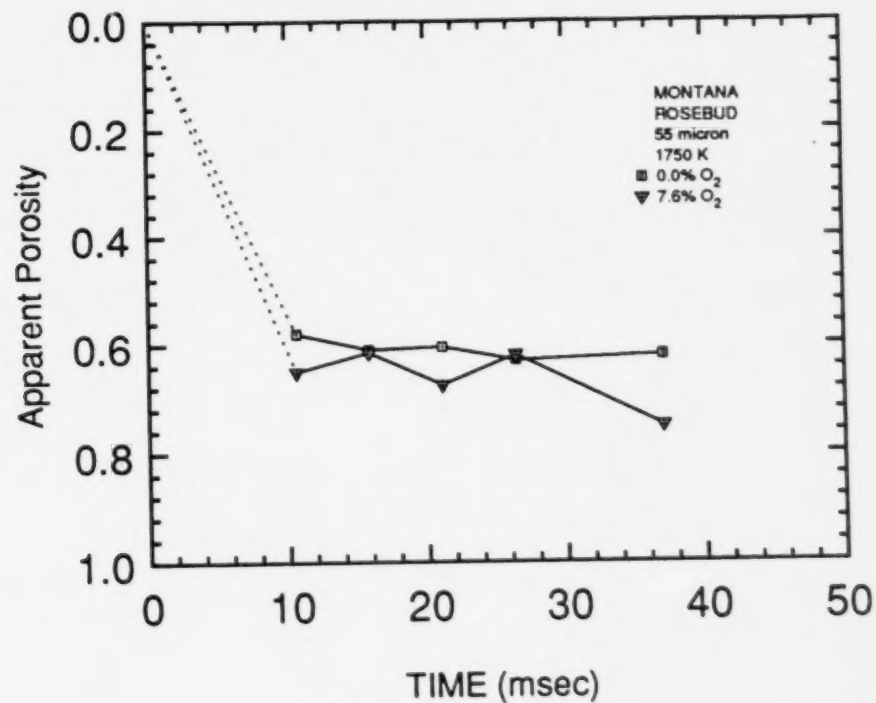


Figure 9. Apparent porosity from cross-section micrographs.

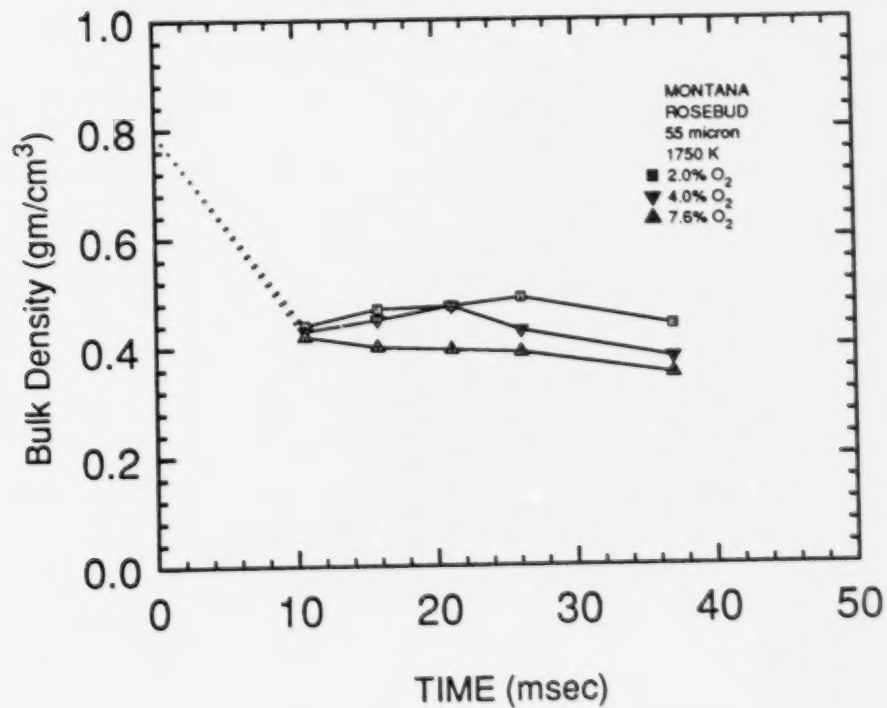


Figure 10. Bulk density measurements.

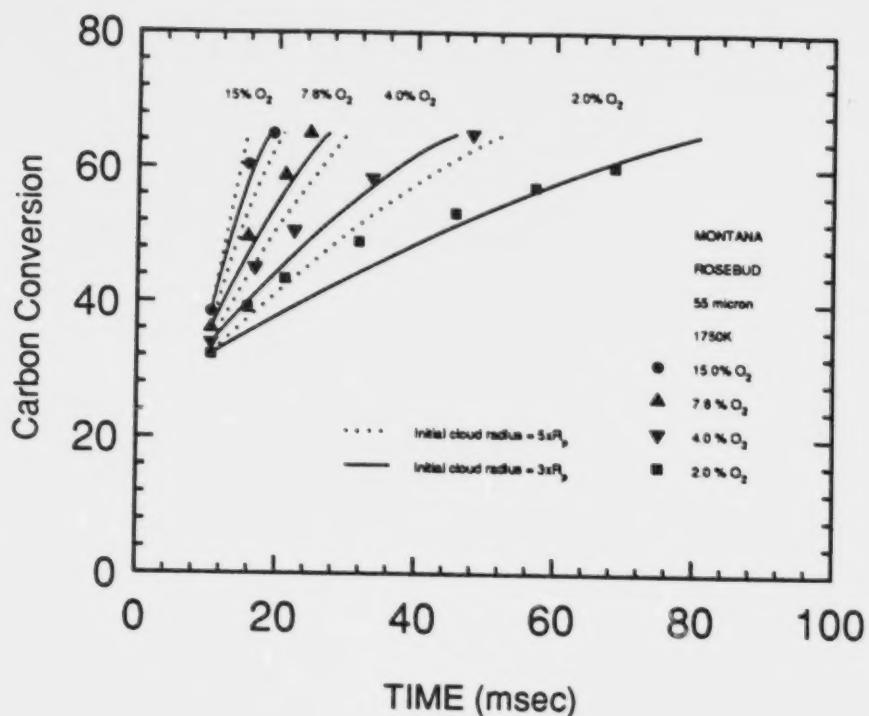


Figure 11. Diffusion-limited combustion model for tar oxidation.

TABLE 1. ELEMENTAL ANALYSIS OF PARTLY-REACTED PARTICLES
(Percentage by mass, on a dry basis)

Res. Time (msec)	Carbon	Hydrogen	Nitrogen	Ash
0.0	59.83	4.13	0.85	9.35
10.1	74.84	1.47	0.95	10.52
15.2	81.32	0.49	0.64	12.64
20.2	73.56	0.77	0.30	15.74
25.3	78.78	0.49	0.43	18.06
35.4	73.44	0.43	0.22	22.17
45.5	62.23	0.49	0.16	30.83
55.6	43.40	0.41	0.10	48.42
65.8	29.50	0.34	0.00	65.39
85.0	22.71	0.13	0.00	75.27

REDUCTION OF NO_x BY FUEL STAGING

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ABSTRACT

Results are reported of theoretical and experimental studies in which natural gas was used as "reburn" fuel for NO_x reduction in a No. 6 fuel oil flame.

A Sandia chemical kinetic code with kinetic parameters of hydrocarbon - NO reactions developed by J.M. Levy and B.R. Taylor at MIT was used to predict chemical species concentrations in the "reburn" zone as a function of residence time, initial NO concentration, gas temperature and fuel equivalence ratio (ϕ).

The fractional reduction of high initial NO concentrations (~ 800 ppm) in the reburn stage is shown to be proportional to the concentrations of CH_i and NH_i species. At high temperatures (2000 K), the abundance of CH_i and NH_i species causes a reduction of NO from 800 ppm to 46 ppm at a ϕ of 1.3. At lower initial NO concentrations (~ 40 ppm), NO formation dominates over its reduction with the result that better reduction of NO is achieved at the lower temperature of 1800 K: for an initial NO concentration of 40 ppm and a $\phi = 1.3$ the exit NO concentrations are 25 ppm and 38 ppm at 1800 K and 2000 K respectively.

For a given gas temperature the CH_i radical concentration increases with increasing fuel equivalence ratio in the "reburn" zone and the fractional conversion of NO to N₂ as a function of ϕ follows the usual trend of showing an optimum at around $\phi = 1.3$. At lower than optimal fuel equivalence ratios the NO reduction becomes strongly temperature dependent. (At $\phi = 1.1$ calculated NO reductions are 18% at 1780 K and 60% at 2000 K). Experimental data obtained in a 1.5 MW No. 6 oil flame with 400 ppm (doped) initial NO concentration and at $\phi = 1.1$ showed good agreement with predictions.

INTRODUCTION

The two combustion process modifications which have been found to significantly reduce NO_x emissions are staging of the combustion air and staging of the fuel. In the combustion air staging technique, conversion of fuel-bound nitrogen (FBN) to N₂ rather than to NO is mainly due to fuel-rich conditions prevailing in the first stage. The degree of FBN conversion to molecular nitrogen is determined by the thermodynamics of the system (temperature, pressure and chemical composition of the gas mixture), and the rates of the reactions in the fuel rich-flame zone (1,2,3,4,5). In practical combustion systems the reactions of FBN and NO may be kinetically constrained and provision of sufficient residence time in the fuel-rich zone is therefore essential for high conversion to N₂ (6,7,8). The nitrogenous compounds in the fuel-rich flame zones may have different origins: they may be pyrolysis products of nitrogen-bearing fuels, products of the fixation of atmospheric nitrogen by hydrocarbon fragments early in the flame (9),

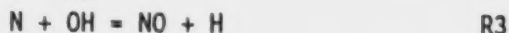
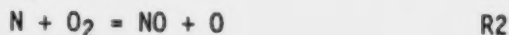
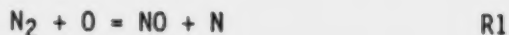
or the result of reactions due to the secondary injection of hydrocarbons into the NO-containing fuel-lean burned gas. In the second process modification, fuel staging, hydrocarbon fragments such as CH₂ and CH react with NO to produce HCN and NH_i compounds (FBN) in a secondary fuel-rich flame zone. The latter species are then reduced to N₂ following the pathway shown in Figure 1.

Recently, experimental and theoretical investigations were carried out to evaluate the effects of fuel type, equivalence ratio, gas temperature of the reburn stage, and the gas mixture residence time within that zone, on NO_x reburning efficiency. Chen et al (10) concluded that NO_x reduction efficiency was best for high NO_x concentration at the end of the primary zone. Residence times of at least 400 ms in the reburn zone were required to favor molecular nitrogen formation. Moreover, natural gas and propane were found to be better than carbon monoxide, hydrogen and coal as reburn fuels. Lanier and Mulholland (11) investigated the reduction of NO_x by natural gas reburning in a two dimensional pilot-scale combustion system. An overall reaction order of 1.5 with respect to NO was observed. When the NO concentration in the primary stage is low, nitric oxide "reburn" efficiency is reduced due to the formation of prompt NO from the reactions of N₂ with hydrocarbon radicals to form HCN and CN species which are then converted to NO through the pathways shown in Figure 1. Other researchers (12) found that extensive reduction of nitric oxide in laboratory scale reactors can be achieved when the combustion products from the primary stage pass through a fuel-rich secondary stage. In a recent study, Taylor (5) tested and validated a model which used a detailed chemical reaction mechanism to predict fixed nitrogen conversion in hydrocarbon-bearing gases. He concluded that several hydrocarbon fragments react with NH_i species and with NO, with CH₂ shown to be the major hydrocarbon radical for reducing NO under the experimental conditions investigated.

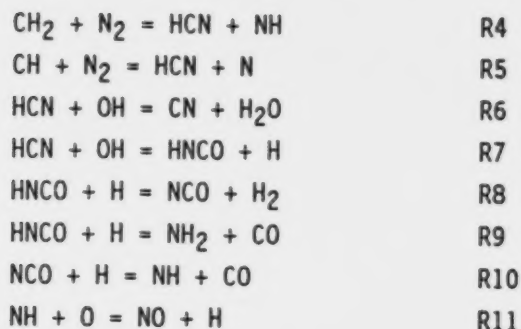
Due to the wide variation in the experimental conditions chosen in the reburn studies, a modeling study is needed to explain the trends of NO_x reburn observed in the experimental work and also to determine the optimum conditions required for NO_x reduction. In an attempt to resolve this issue, mathematical modeling studies which include NO_x reburn chemistry were carried out.

NO_x REBURN CHEMISTRY

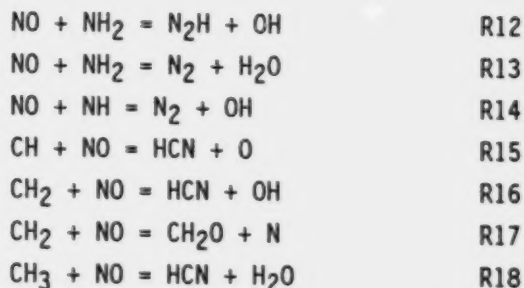
The experimental results reported in the literature show that NO_x reduction efficiency in the reburn zone can be influenced by both nitric oxide formation and destruction processes. Consequently, inclusion of both processes in modeling of the reburn zone is essential for determination of the conditions under which the destruction mechanisms will predominate. The formation route involves the reactions of molecular nitrogen and N atoms with OH, O atom and O₂ to form NO (Zeldovich NO).



NO can also be produced through the fixation of molecular nitrogen. In this pathway, molecular nitrogen reacts with hydrocarbon radicals such as CH and CH₂ to form HCN and CN. These then react with O, OH, and H atoms to form NH₂ and NH₃ species which are subsequently converted to NH and N by hydrogen abstraction. The N and NH radicals then react with O₂, O, or OH to produce NO (prompt NO); reactions R4 through R11 illustrate the steps that lead to the formation of NO through this mechanism.



A consideration of the destruction routes of NO shows that NO can be destroyed in two ways. It can be reduced either by reacting with ammonia (NH_3 , N) species to form molecular nitrogen (R12-R14) or by reacting with hydrocarbon radicals such as CH and CH_2 to produce hydrogen cyanide (R15-R18) which in turn is converted to NH_3 through reactions R6 to R10. The ammonia species thus formed can subsequently reduce NO to N_2 .



To be able to design an effective strategy of NO reduction, the effect of temperature, fuel equivalence ratio and reaction time upon the speed of the various processes which either form or destroy NO, must be evaluated.

This was achieved by numerical calculations made on a plug flow model which included the above reaction mechanisms.

NO_x NUMERICAL ANALYSIS

Numerical calculations were carried out using a chemical kinetic code developed at Sandia National Laboratory (13) coupled with a differential equation solver developed at Lawrence Livermore Laboratory (14). The code solves the initial value problem for stiff or non-stiff systems of first order differential equations. The equations considered in this study were the mass species equations. By feeding a reaction mechanism, a temperature profile, and species initial mole fractions into the program, equation 1 can be solved for the different species considered in this study.

$$\frac{dY_k}{dt} = \frac{\dot{w}_k w_k}{p} \quad (k = 1, \dots, N) \quad (\text{E1})$$

where

Y_k mass fraction of species k

p total mass density

$\dot{w}_k$ the molar production rate of species k

w_k the molecular weight of species k

MODELING RESULTS

A practical fuel-staged combustion system can be comprised of several zones, the first of which would have fuel-lean stoichiometry. In the so-called reburn stage, secondary fuel is injected to change the stoichiometry to fuel-rich. Further downstream in a third stage the remaining combustion air is introduced to mix with the combustion products leaving the first two stages and reduce the overall equivalence ratio to less than unity.

The present calculations deal with an idealized second-stage, in which the secondary fuel (CH_4) is assumed to be instantaneously mixed with the first stage combustion products. The initial NO concentration, temperature and equivalence ratio in this reburn-stage were varied over wide ranges, and the subsequent combustion chemical composition of the reacting mixture was evaluated numerically under conditions of constant temperature.

The input conditions for the numerical calculations performed are listed in Table 1. Twelve runs were made, with initial NO_x concentration, fuel equivalence ratio and temperature all being varied.

Two additional runs at a fuel equivalence ratio of 1.3 were done using a reaction set which omitted reactions R15-R18 from the destruction mechanism of NO . The input conditions for these runs (13,14) are the same as those for runs 1&2 respectively. The results obtained from the numerical calculations are discussed next.

EFFECT OF TEMPERATURE

In Figures 2 and 3 NO , NH_3 , HCN and total fixed nitrogen (T.F.N.) concentrations are plotted as a function of residence time in the plug flow reactor for two levels of initial NO mole fractions (800 vs. 40 ppm). For a high initial NO concentration (800 ppm), maintaining the reburn reactor at 2000 K instead of 1700 K has the benefit of converting a higher fraction of the NO exiting the first combustion stage into molecular nitrogen. A reduction from around 800 ppm to 46 ppm at a ϕ of 1.3 is predicted for a "reburn" stage temperature of 2000 K. Figure 4 shows that a reduction of NO is still observed even at ϕ of 1.1 if the temperature is maintained at 2000 K; a reduction of 500 ppm is calculated. As the NO concentration in the feed stream decreases, the benefit of operating the reactor at 2000 K diminishes. This result is in agreement with the results obtained in experimental investigations reported by other workers (10,15). The numerical simulation showed that a higher reduction efficiency was achieved by running the reactor at 1800 K instead of 2000 K if the NO concentration in the feed stream was 100ppm or lower. Maintaining the "reburn" zone at an equivalence ratio of 1.3 serves the purpose of initiating the reduction process of NO through reactions R15-R18. At the considered temperatures of 2000 K, 1800 K and 1700 K, the rate of NO destruction through R15-R18 is fast. The HCN formed in this process is then converted to ammonia. If the temperature is high, NH_3 is depleted by reacting with NO or with other NH_i species to produce molecular nitrogen. Otherwise, it will build up in the reactor as shown in Figures 2 and 3, and this unconverted NH_3 will eventually be oxidized to NO in the third lean stage. Consequently, when both the NO concentration and the temperature are high the total fixed nitrogen entering the reburn stage can be effectively converted to molecular nitrogen.

For the case of low initial NO_x concentration, both the NO formation mechanism due to reaction of molecular nitrogen with hydrocarbon fragments, and its formation through the Zeldovich route become important. If the initial NO_x concentration is

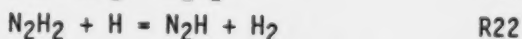
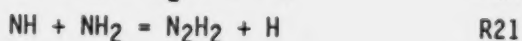
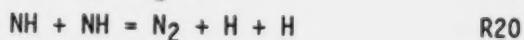
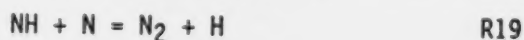
zero, the model predicts the formation of 15 ppm of NO at 2000 K and only 3₃ppm at 1700 K at a fuel equivalence ratio of 1.3. At short residence times ($\sim 10^{-3}$ sec), a high temperature (~ 2000 K) results in a fast rise of CH₂ radical concentration and in turn an early depletion of NO (Figure 5). When the CH₂ radical concentration becomes low, thermal NO builds up in the reactor, with the end result of having a zero reduction efficiency for the case of low primary NO_x concentration. At lower temperatures (1800 K), on the other hand, very little thermal NO is formed and thus all the NO leaving the primary stage is converted to HCN and then to NH₃. The ammonia species so produced are slowly converted to molecular nitrogen. This implies that at low concentrations of NO the formation chemistry becomes dominant over the NO destruction process at high temperature, and thus a lower temperature provides a better NO reduction efficiency.

In summary, the computer calculations show that it is not always correct to assume that high temperatures are needed for significant reductions of NO_x. It can be concluded that for a particular concentration of NO entering the "reburn" stage, an optimum temperature can be chosen for the maximum reduction of NO_x. It is surprising that the temperature range so required agrees well with that in practical boiler combustion processes (16).

EFFECT OF FUEL EQUIVALENCE RATIO

As mentioned earlier, the initiation of the NO reduction process is mainly due to the reactions of NO with CH_i and ammonia species. Any investigation addressing the effect of fuel equivalence ratio on NO reduction has to be focused on determining the variations of CH_i and ammonia species as a function of equivalence ratio. The importance of the presence of CH_i on NO_x reduction was evaluated by solving the plug flow model equations while including reactions R15-R18 in the destruction mechanism in one case, and omitting them from the other. The results obtained are shown in Figure 6.

It is noteworthy that the inclusion of reactions R15-R18 in the destruction mechanism is essential for predicting the NO_x reduction trends that are observed in the various experimental studies cited above (10,15,16). The high concentrations of CH₂ resulting from the fuel-rich conditions (Figure 7) in the reactor can speed up the reduction process of NO_x, especially at the lower temperature (1700 K). At this temperature NO reduction through its reaction with NH_i is not significant. Consequently, the route in which CH_i reacts with NO provides the means for producing ammonia species which can either reduce NO to N₂ or can be reduced directly to molecular nitrogen by reactions R19-R23.



At 2000 K, on the other hand, the reaction of NO with NH_i becomes significant and can account for more than 50% of the NO_x reduction.

At leaner conditions ($\phi \sim 1.1$) the concentration of CH₂ decays very quickly at short residence times and thus its role in reducing NO diminishes (Figure 7). The only route available for NO reduction is via its reaction with ammonia species.

In conclusion, at high equivalence ratios relatively low temperatures (~ 1700 K) are required for a significant reduction of NO_x, whereas at low equivalence

ratios ($\phi = 1.1$) high temperatures (2000 K) are more favorable for an effective reduction of NO_x .

EXPERIMENTAL EVALUATION OF NO_x REBURN AT $\phi = 1.1$

For a comparison with model calculations, experiments were carried out at the MIT Combustion Research Facility in which a 1 MW No.6 fuel oil turbulent diffusion flame was doped with NO in order to establish a pre-specified flux of NO entering a fuel-rich "reburn" combustion stage. In these experiments the reburn fuel was natural gas and the fuel equivalence ratio in that stage was 1.1. The total thermal input was maintained at 1.5 MW. The axial positions of the secondary fuel and air injection systems were chosen so that a lean-rich-lean configuration would result. The configuration chosen for this set of experiments is shown in Figure 8. Mass fluxes of NO_x were determined from velocities and measured NO_x radial profiles.

The reduction efficiency, which is defined as:

$$1 - \frac{\text{NO flux leaving rich stage}}{\text{NO flux entering rich stage}}$$

is plotted as a function of the NO concentration entering the rich "reburn" stage in Figure 9. For the purpose of comparing the model calculations with the experimental results, the calculations were made at $\phi = 1.1$ and 1.3 and at three temperature levels (1700, 1780, and 2000 K). In the experiment, the temperature in the second stage was close to 1780 K. As can be seen from Figure 9, very good agreement exists between model calculations and experimental data for a wide range of initial NO concentrations. It is also of interest that even for a relatively low value of the fuel equivalence ratio in the second stage ($\phi_s = 1.1$), 18% reduction of NO was obtained for an initial NO concentration of 500 ppm.

CONCLUSIONS

- o Total fixed nitrogen reduction in the fuel-rich "reburn" stage is most effective when the inlet NO concentration is high ($\text{NO} > 100$ ppm).
- o A fuel equivalence ratio of 1.3 is favorable for the reburn stage because of the relative abundance of CH_i and NH_i species, but the model shows that NO_x reduction is possible even at $\phi = 1.1$. In this latter case, however, high gas temperature (~ 2000 K) is required.
- o Under fuel-rich conditions, and an initially high NO concentration, nitric oxide conversion to HCN is rapid due to the fast reaction rates of NO with CH_i . The conversion rates of HCN and NH_i to N_2 , on the other hand, are temperature dependent. Consequently, high temperatures are required to insure high NO_x reduction efficiencies.
- o Thermal NO formation in the reburn stage plays a significant role in reducing the efficiency of NO_x reburn if the initial NO_x concentration in that stage is low (~ 40 ppm). Since the rate of formation of NO through this mechanism is highly temperature dependent, a temperature of around 1700 K is favored in the reburn stage when the primary stage NO concentration is low (~ 40 ppm).
- o Experimental data obtained in a 1.5 MW No. 6 fuel oil flame with 400 ppm (doped) initial NO concentration and at $\phi = 1.1$ showed good agreement with numerical predictions.

ACKNOWLEDGEMENTS

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Table 1
Input Conditions for Numerical Calculations

Run No.	NO _x Initial Concentration ppm	Equivalence Ratio of Reactor	Temperature of Reactor (K)
1	793	1.3	2000
2	793	1.3	1700
3	40	1.3	2000
4	40	1.3	1800
5	808	1.1	2000
6	808	1.1	1700
7	407	1.1	2000
8	407	1.1	1700
9	102	1.1	2000
10	102	1.1	1700
11	40	1.1	2000
12	40	1.1	1700
13*	793	1.3	2000
14*	793	1.3	1700

*Reaction CH₄ + NO not included in mechanism.

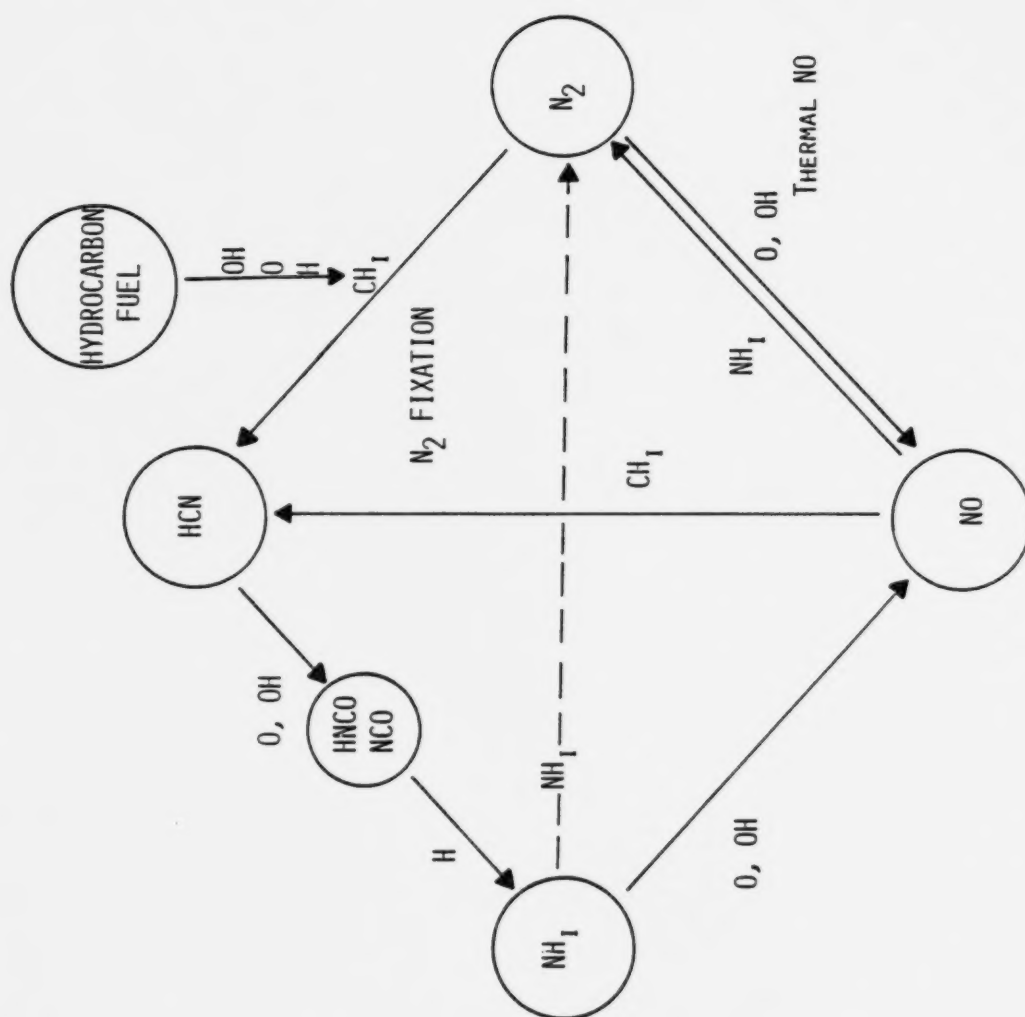


FIGURE 1. SCHEMATIC OF THE FORMATION AND DESTRUCTION MECHANISMS OF NO.

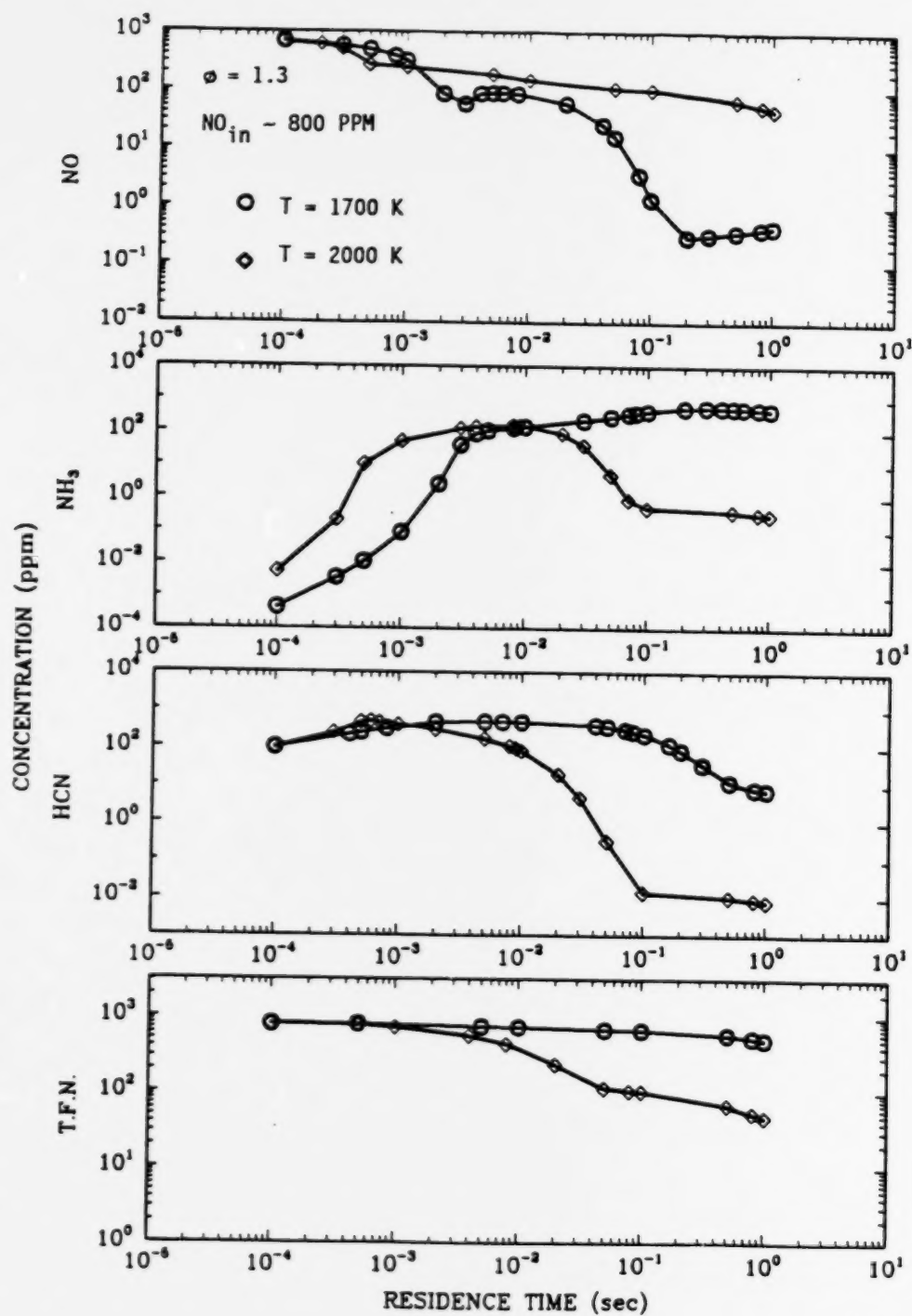


FIGURE 2. EFFECT OF REACTOR TEMPERATURE ON NO_x REBURN

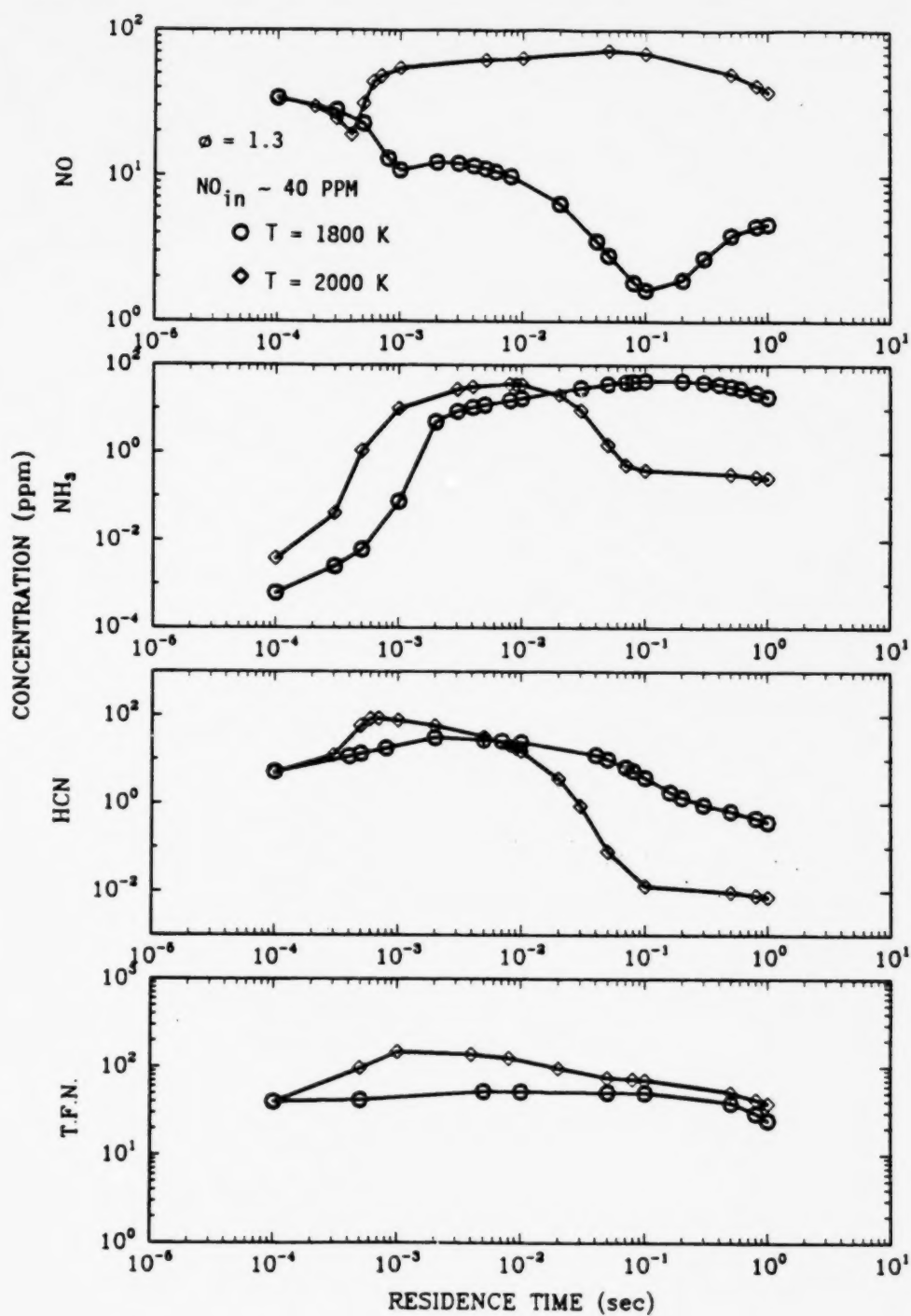


FIGURE 3. EFFECT OF REACTOR TEMPERATURE ON NO_x REBURN

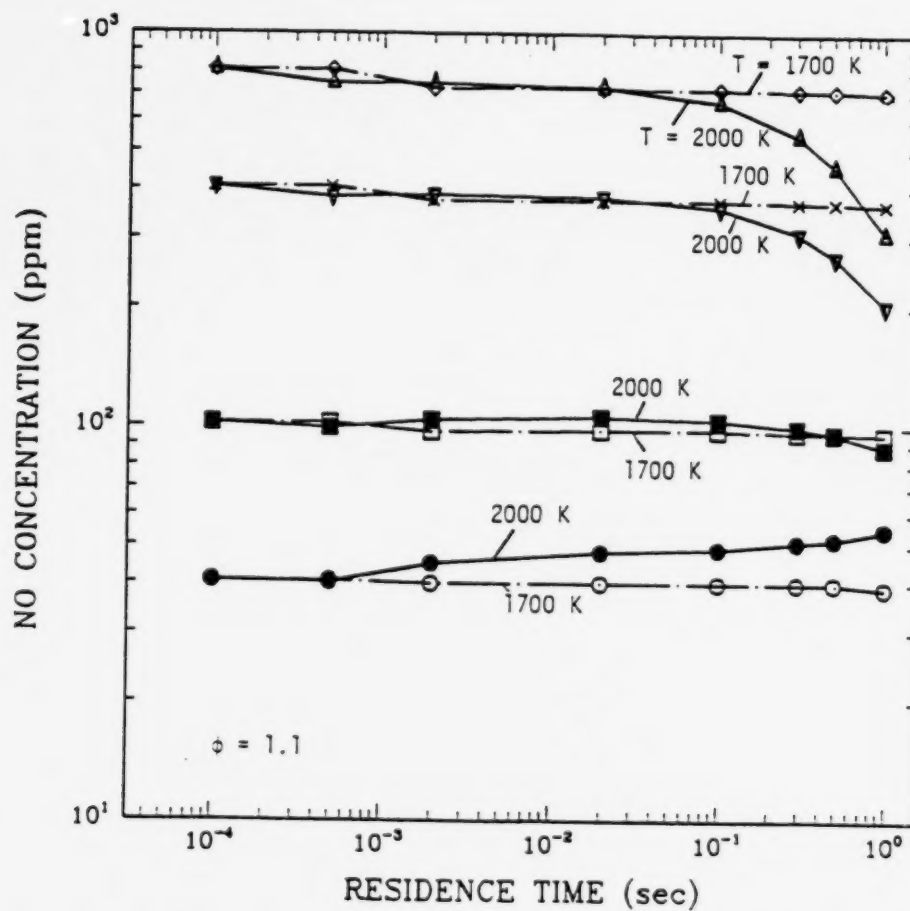


FIGURE 4. PREDICTIONS OF THE EFFECT OF TEMPERATURE ON NO_x REDUCTION IN A FUEL RICH PLUG FLOW REACTOR ($\phi = 1.1$).

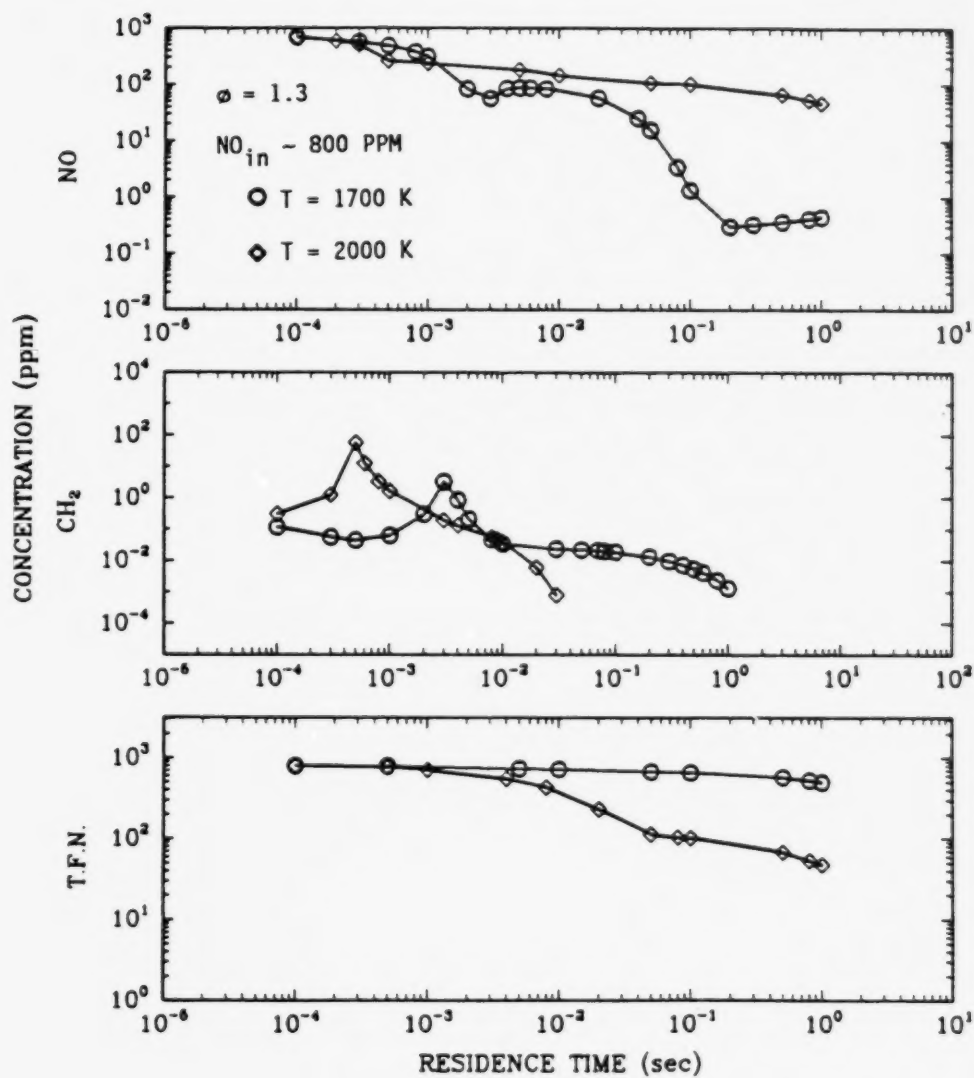


FIGURE 5. EFFECT OF REACTOR TEMPERATURE ON NO_x REBURN

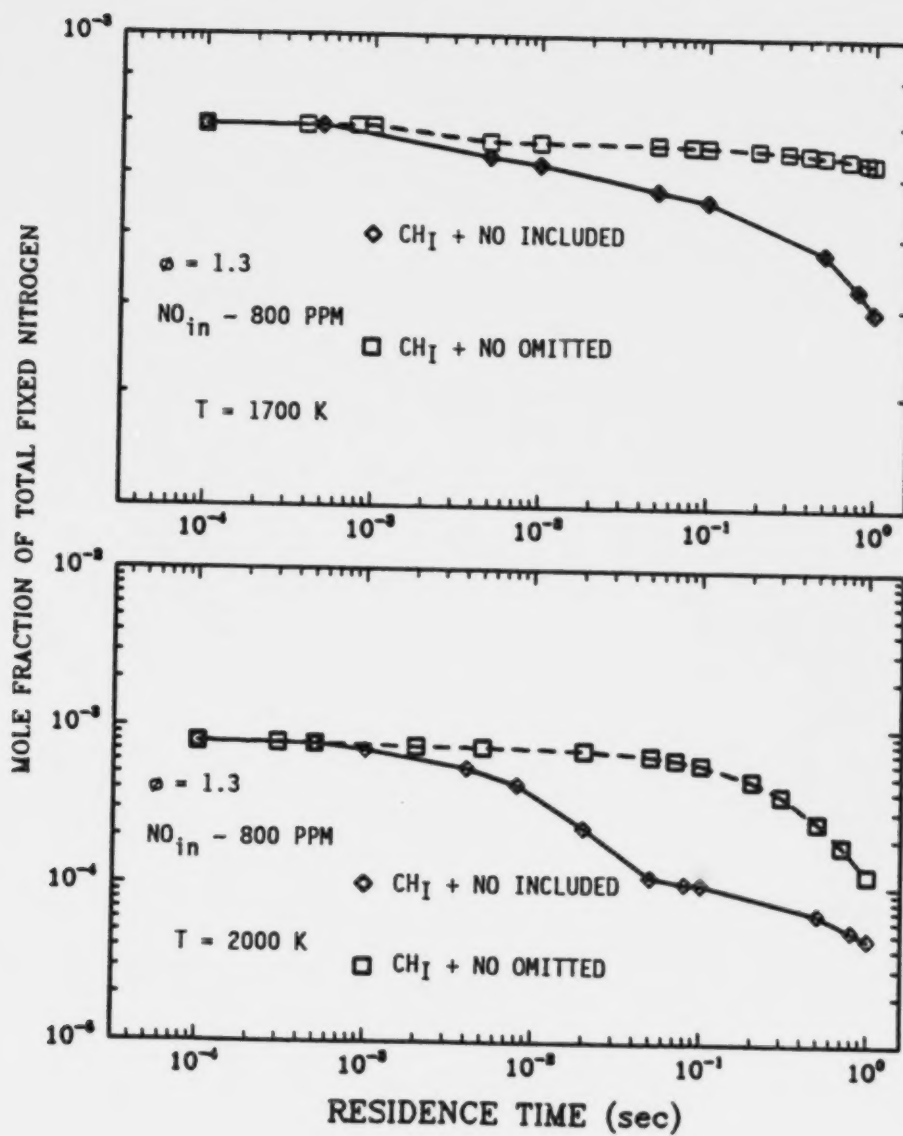


FIGURE 6. EFFECT OF THE REACTIONS OF HYDROCARBON RADICALS WITH NO ON THE REDUCTION OF TOTAL FIXED NITROGEN

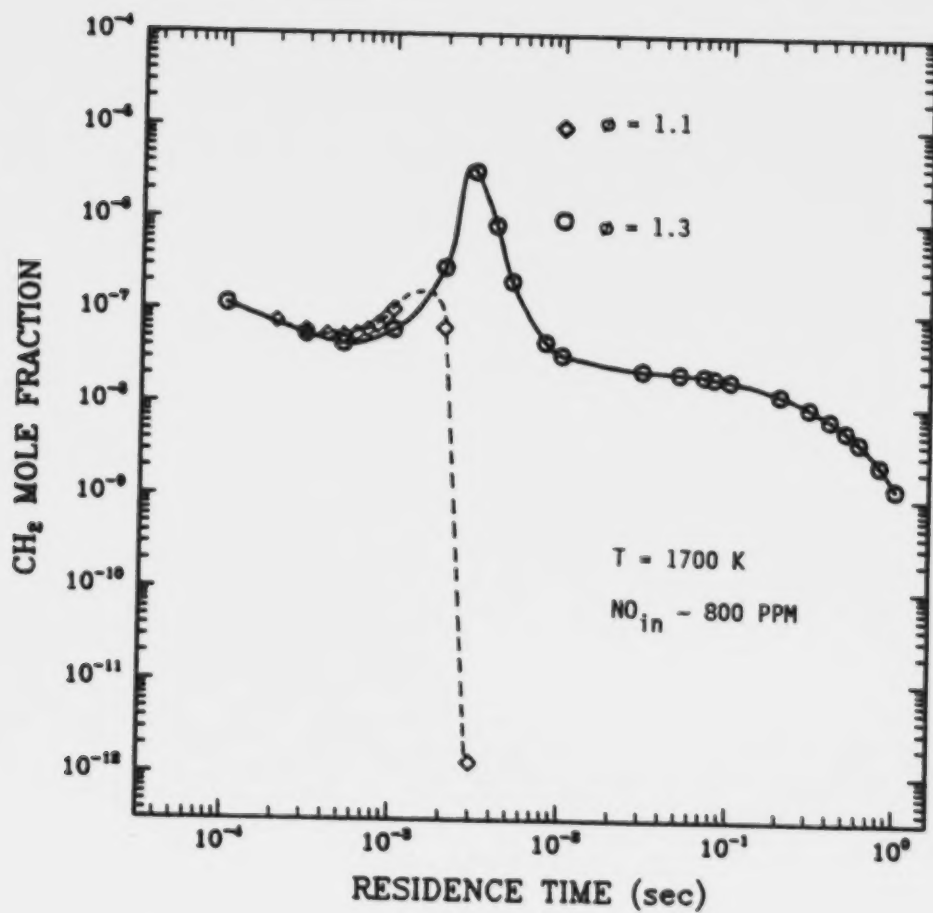


FIGURE 7. EFFECT OF REBURN STAGE EQUIVALENCE RATIO ON CH_2 MOLE FRACTION

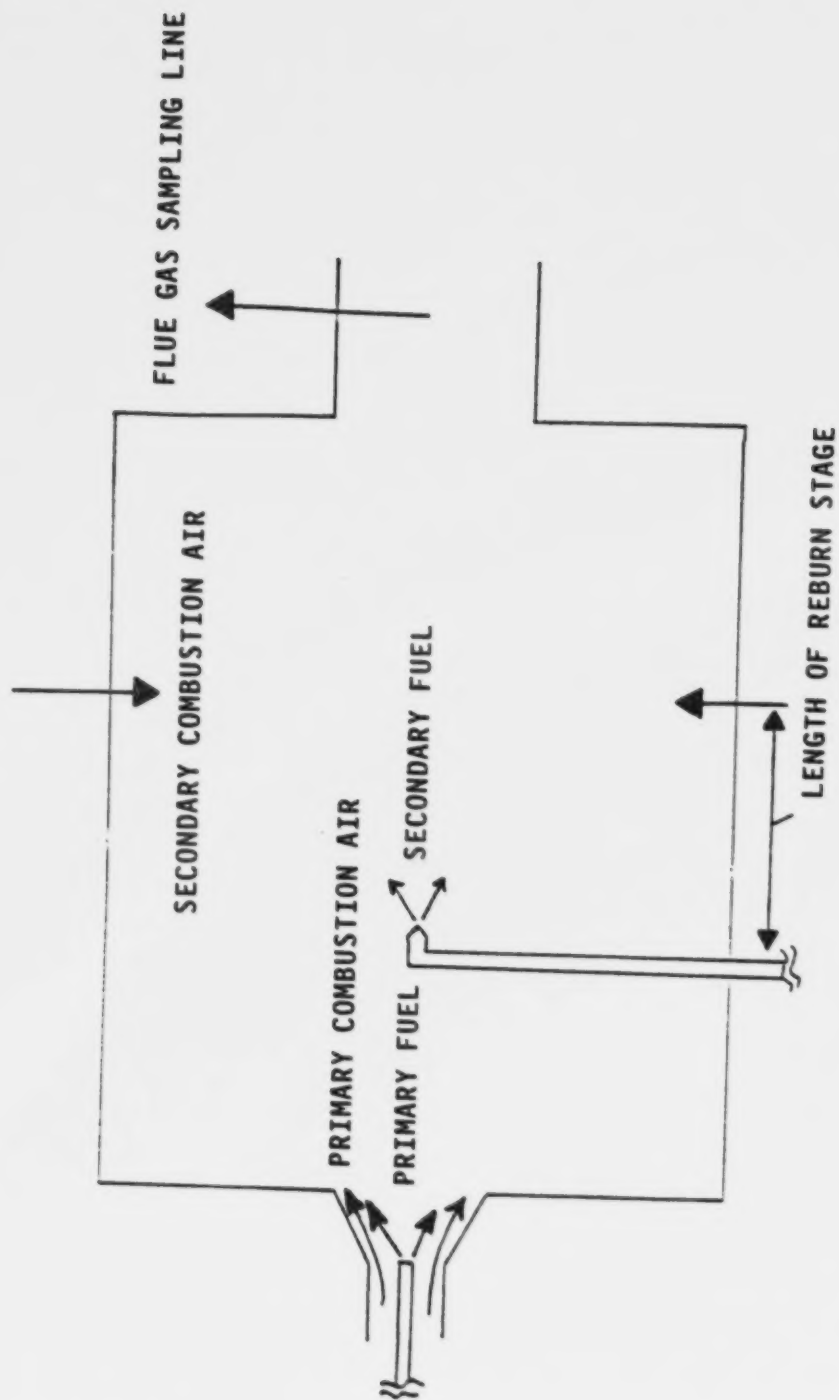


FIGURE 8. SCHEMATIC OF THE FURNACE CONFIGURATION USED IN THE STUDY

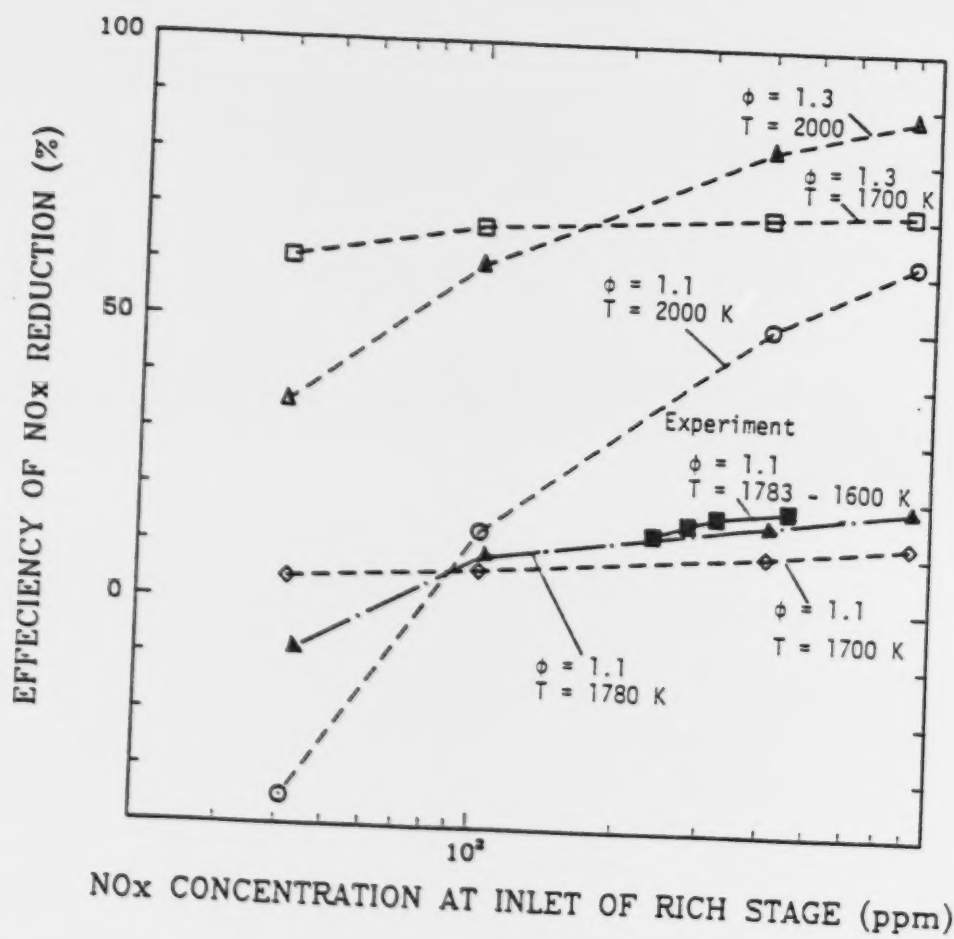


FIGURE 9. A COMPARISON OF THE EXPERIMENTAL RESULTS AND MODEL PREDICTIONS FOR DIFFERENT INITIAL NO_x CONCENTRATIONS AT (ϕ - 1.1, 1.3, T = 1700, 1780, & 2000 K)

FUEL BOUND NITROGEN EVOLUTION DURING THE DEVOLATILIZATION
AND PYROLYSIS OF COALS OF VARYING RANK

by

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ABSTRACT

The near-term use of coal for power generation involves the development of low NO_x burners for retrofit applications or the design of new boiler systems. Intermediate and long-term applications propose using dry or slurried micronized coal feeds in modular, load-following high intensity combustion systems. All systems anticipate a form of stoichiometric staging of the micro-scale combustion process to obtain acceptable levels of NO_x emissions. However, maximizing carbon burnout while minimizing NO_x formation in these systems will require the formulation of quantitative models of the micro-scale combustion process of coals of varying rank characteristics. The complexity of the processes involved will necessitate models more empirical and phenomenological than mechanistic, but will need to take into account the significant variation in nitrogen evolution pathways with coal type.

This communication reports results of an investigation of the nitrogen evolution behavior of a range of coal ranks in a variety of heating conditions and the initial formulation of a kinetic model of coal nitrogen devolatilization. With respect to the total mass fraction of coal nitrogen volatilized during transient heating of particles to 1000 C, the evolution of fuel bound nitrogen appears relatively rank insensitive in moderate heating rate conditions for high volatile bituminous coals and lower ranks. The mass fraction of nitrogen evolved follows the mass fraction of coal volatilized and, under conditions where secondary reactions of tar are minimized, the distribution of parent coal nitrogen between tar and light gases follows the distribution of parent coal mass between these volatile types. The distribution of coal nitrogen in volatile types varies as the distribution of coal mass between the volatile types. For medium volatile and higher rank coals, the mass fraction of nitrogen evolved during particle heating to 1000 C varies as the volatility of parent coal and is therefore rank sensitive. However, in moderate heating rate conditions, the distribution of parent coal nitrogen between volatile types continues to follow the distribution of parent coal mass between these types.

The susceptibility of devolatilization produced tar species to secondary pyrolysis reactions varies significantly with coal rank characteristics. Secondary reactions of tar occur within the devolatilizing particle, in the boundary layer around the particle, and in the free stream. High temperature secondary pyrolysis reactions of tars occurring in fuel rich conditions result in the release of tar-bound nitrogen to the light gas component of the volatile yield, primarily in the form of HCN. The high temperature secondary

reaction network leading to the production of cyanide species also produces acetylene, ethylene, and carbon monoxide and appears to commence the onset of soot production. The secondary reaction network for tars commences at particle or gas temperatures of 900 C with a strong temperature and coal rank dependence. The formation of light gas nitrogen species, NO_x precursors, is strongly rank dependent because the temperature sensitivity of secondary reactions of the heavy hydrocarbons formed at relatively low particle temperatures, 300 - 600 C, varies with the mix of hydrocarbon species present in the parent coal, that is the rank characteristics of parent coal. Progress in the formulation of a rank dependent model of nitrogen evolution is discussed.

INTRODUCTION

The near term use of coal for power generation involves the development of low NO_x burners for retrofit applications or the design of new boiler systems. Intermediate and long term applications propose using dry or slurried micronized coal feeds in modular, load-following high intensity combustion systems. All systems anticipate a form of stoichiometric staging of the micro-scale combustion process to obtain acceptable levels of NO_x emissions. However, maximizing carbon burnout while minimizing NO_x formation in these systems will require the formulation of quantitative models of the micro-scale combustion process of coals of varying rank/chemical characteristics. Of particular interest is the coupling between the nitrogen devolatilization characteristics of a particular coal and heating conditions. This communication reports results of an investigation of the nitrogen evolution behavior of a variety of coal types in a range of heating conditions and the initial formulation of a phenomenological kinetic model of coal nitrogen devolatilization.

OBJECTIVES

The objectives of this work are: 1.) to quantitatively compare the nitrogen devolatilization behavior of a range of coal types; 2.) to determine the degree of coupling among heating conditions and coal characteristics in determining nitrogen evolution patterns; 3.) to establish a phenomenological framework specifying the major physical and chemical processes that determine the transformation of fuel-bound nitrogen to NO_x precursors in a combustion environment; 4.) to relate the phenomenology of fuel-bound nitrogen evolution to coal structure parameters.

TECHNICAL APPROACH AND ASSUMPTIONS

The complexity of the fuel nitrogen evolution process arises from both the significant variations in structural characteristics with coal type and geologic origin and the intimate coupling among heat transfer parameters and intrinsic coal characteristics to produce a given devolatilization product distribution. The complexity necessitates explicit formulation of assumptions and technical approach. The coal structure "pseudo-assumptions" are: 1.) the parent coal nitrogen is uniformly distributed, on a mass fraction basis, throughout the mix of molecular types present in the coal structure; 2.) parent coal nitrogen is found primarily in ring structures - aromatic (pyridine or quinoline type structures) or alicyclic (pyrrole types); 3.) the fraction of parent coal nitrogen found in aromatic ring structures increases as does the rank characteristics of the coal. These assumptions are called "pseudo" because there is some analytical evidence in support of these assumptions, but quantitative measures as a function of coal rank characteristics are not available.

The assumptions imply that the distribution of parent coal nitrogen in intermediate devolatilization products would vary significantly with heating conditions for a given coal or with coal type for a given set of heating conditions.

The on-going fuel nitrogen evolution studies performed in this laboratory employ three different reactor systems, having widely varying heat

transfer characteristics. As many as twenty coals have been investigated in an attempt to formulate a comprehensive understanding of coal-nitrogen to NO_x precursor pathways.

SAMPLE CHARACTERIZATION

Table I lists the elemental composition of the fourteen "core" coals utilized in this investigation. These samples span a wide range of coal rank and geologic provinces. Figure 1 displays the location of these samples on a coalification band plot. As is well known, the H/C ratio of coals remains relatively constant from the lignite through the high volatile bituminous coal range. And there is no clear trend in total hydrogen composition with coal rank (Figure 2). As indicated in Figure 3, there is a regular decrease in total sulfur and oxygen content with increase in coal rank, as estimated by carbon content.

Figure 4 displays the infrared absorbance spectra of approximately 1 mg of finely ground (mass mean 1 - 4 microns) high volatile bituminous coal uniformly dispersed in 300 mg of KBr. The major absorption bands are indicated and a key to interpretation given in Table II. A sample with less than 1% mineral matter was selected to avoid the problem in deconvoluting the effects of mineral matter absorption bands in interpreting the organic matrix absorption bands. The arbitrarily chosen baselines associated with a particular functional group are indicated in Figure 4. After subtracting the bands associated with functional group concentrations, the remaining broad background absorbance from 2000 cm⁻¹ to 4000 cm⁻¹ is designated "subtracted background" area. This area is primarily identified with the concentration of condensed aromatic ring structures present in the organic matrix of the coal sample. Although Mie scattering calculations indicate scattering contributions are present the total effect on extinction of the infrared beam is secondary to true sample absorbance or intraparticle scattering. Figure 5 displays a plot of background absorbance versus coal rank as estimated by carbon content of a particular sample.

Mineral matter free absorbance spectra for each sample are generated by establishing sample specific mineral matter absorbance spectra for each sample. This is accomplished by storing the absorbance spectra of specific gravity separated samples of each coal and computer subtraction of the two spectra. The residual spectra gives a semi-quantitative spectra of the sample specific mineral matter absorbance bands which can then be subtracted from the whole coal spectra to give the organic matrix absorbance spectra alone. Figure 6 displays the "total" organic functional group absorbance as a function of carbon content of the samples. Figures 7, 8 and 9 display the aliphatic hydrogen, hydroxyl hydrogen, and aromatic hydrogen absorbance bands for the fourteen core coals as a function of carbon content. Figure 10 is a plot of aromatic hydrogen absorbance versus hydroxyl hydrogen absorbance for each of the coals.

Inspection of the elemental compositions and infrared absorbance characteristics of each sample indicates, as is well known, no single rank parameter can give a clear indication of the complex mix of chemical species that constitute the organic matrix of a particular coal sample. For example, the carbon contents and hydrogen contents of samples 5, 6 and 10 are similar while the total sulfur and oxygen level of sample 10 (Kentucky #9) is measured as greater than that of samples 5 and 6 (Western bituminous) coals.

Background absorbance analysis indicates as much greater concentration of condensed aromatic ring structures in sample 10 relative to 5 and 6 (See Figure 5). In addition the Western bituminous coals display a greater total functionality (Figure 6) and much greater aliphatic hydrogen absorbance than the Appalachian province bituminous coal. Aromatic and hydroxyl hydrogen absorbance areas are similar but Appalachian province coals generally have more clearly resolved absorbance maxima than the Rocky Mt. bituminous samples.

IMPLICATIONS OF SAMPLE CHARACTERISTICS TO NITROGEN DEVOLATILIZATION

Since the distribution of the parent coal nitrogen is assumed to mirror the distribution and type of aromatic ring structures in the parent coal, one would expect widely varying transient nitrogen devolatilization patterns with change in coal type. The formation of immediate NO_x precursors (HCN, NH₃ and nitrogen radical fragments) from a devolatilizing/pyrolyzing coal particle is the result of pyrolysis fragmentation of molecular units present in the parent coal particle. This fragmentation can take place within the transiently heating coal particle, in the boundary layer around the particle, or in the free stream surrounding the devolatilizing coal particle. The transient distribution of coal nitrogen as an element in a heavy hydrocarbon (tar precursor, evolved tar) species or as a light gas species depends on the thermal stability of the molecular mix in the parent coal source.

EXPERIMENTAL SYSTEMS CHARACTERIZATION

The significant influence of transport characteristics on coal devolatilization necessitates characterization of reactor heat transfer properties in some detail. Figure 11a displays the power density regimes required for a given heating rate of inert, spherical particles having thermal capacities equivalent to coal. Also shown are the range of power density capabilities of the heated grid flash lamp and entrained flow reactors employed in this investigation. The heated grid employed in this investigation generates power densities of 1-6 watts/cm² at grid temperatures between 600 K and 1200^oK. The flash lamp system generates power densities, in the form of transient irradiance levels. Time averaged levels from 200 watts/cm² to greater than 700 watts/cm² were employed. Entrained flow reactors are generally operated in the 10-100 watts/cm² regime. Figure 11b shows heat transfer conditions appropriate to coal combustion systems. Final particle temperatures of 1000^oK or greater can be obtained in each system, but for significantly different transient times. In addition, heavy hydrocarbons evolved in each system experience widely varying environments. Heavy hydrocarbons evolved in the grid or flash lamp systems are quenched once they are transported through the particle boundary layer. In the entrained flow reactor these species evolve into a hot environment wherein they undergo secondary pyrolysis reactions.

UTRC HEATED GRID (HG)

The heated grid experiments are conducted by imposing a controlled voltage across a folded No. 325 mesh stainless steel screen. The screens are prefired, then loaded with 20-30 mg of coal by evenly distributing the coal between the folds of the screen. Simultaneous, real time measurements of applied voltage across the screen, current flow, and temperature of the screen are made by a rapid data acquisition system. The grid, char and tar are quenched by impingement of high velocity helium jets on the grid at the end of

the heating program. The light gases evolved are measured by a FT-IR gas analysis system attached directly to the heated grid cell. A schematic of the heated grid system is shown in Figure 12. Typical temperature trajectories and power density fields created by the heated grid system in various ambient conditions are illustrated in Figures 13 and 14. The power density fields in vacuum conditions consists mainly of irradiance, whereas in the presence of ambient gases there can be a significant gas conduction component. The magnitude of the gas conduction component varies significantly with the thermal conductivity of the gas, as expected. The power density fields were determined by synchronously measuring delivered current and voltage while measuring the temperature of the screen at pseudo steady-state conditions, and normalizing with respect to screen surface area. Power density dissipation factors are reported for unloaded screens. Such measurements are also made with samples in place. Depending on the heat transfer characteristics and heat capacity properties of the sample relative to the screen and ambient gas, the sample can significantly couple to the local power density field. Such coupling has been demonstrated to change the observed temperature trajectory of the screen relative to an unloaded screen area. With respect to this communication, the main element of interest is the magnitude of the power density levels established by the heated grid system in the 600°K to 1000°K screen temperature regime, the temperatures of tar formation and evolution in such heating systems.

UTRC FLASH LAMP (FL)

A schematic of the flash lamp reactor is illustrated in Figures 15a and b. The time resolved pulse shape of the flash pulse is shown in Figure 16. Under the range of capacitor voltage levels used in this investigation and with the particular match of capacitor voltage levels and driving circuit the pulse did not vary significantly. The magnitude of the irradiance level delivered to the inside of the reactor was controlled by varying the neutral density filter and/or the capacitor bank voltage levels. The real time irradiance levels of the flash pulse were monitored by fast response pyroelectric detectors. The detectors employed were calibrated with NBS irradiance standard lamps and a NBS traceable radiometer system used in conjunction with a chopped Argon ion laser. Pyroelectric detectors have a nearly constant responsivity with respect to wavelength from the UV to IR spectral regimes. Because of the possibility of inducing photochemical reactions with the UV component of the flash pulse, the reactors employed were pyrex, as were the neutral density filters. The delivered radiation is characterized by wavelengths ranging from 0.4 to 2.0 microns with peak intensities between 0.8 and 1.1 microns. Characteristics of the transient pulses are indicated in Table III.

UTRC FLOW REACTOR

Phase Separation

Figures 17, 18, and 19 display the overall reactor design, aerosol-char separation device and the aerosol and char separation trains. Approximately 75% of the total reactor flow is diverted to the aerosol train. Both the cyclone (char) train and impactor (aerosol) train are followed by final filters. These filters consist of porous metal disks to ease in removal of tar species. Approximately 90% of the tar mass appears to collect on the final filters, with some deposition on stages 7 and 8 of the impactor train.

SEM analysis of the impactor and cyclone stages as well as the final filters reveal the phase separator extracts particulates and aerosols less than 2 microns from the particulate flow at 75% gas flow removal. Tar material deposited on the final filter substrates consists almost entirely of condensed heavy hydrocarbons having no particulate boundary structure. Particulate material is efficiently removed by the impactor and cyclone stages.

GAS ANALYSIS - MULTIPASS IR CELL SYSTEM AND CALIBRATION

As noted in Figure 19 the total reactor flow is recombined after the separated flows pass through the final filters. This total flow is then passed through a multipass, selectable path length gas cell attached to a Fourier Transform Infrared Spectrometer (FT-IR). The nature and composition of the devolatilization/pyrolysis gas yields are determined by comparison to calibration spectra and matching peak heights to calibration curves. Non-interfering wavelengths, that is, wavelength peaks specific to each gas are used in determining the calibration concentration curves.

The multipass IR cell is calibrated statically and with flow for purposes of cross checking calibration curves developed for each gas. Calibration curves have been developed for CH₄, CO, C₂H₂, C₂H₄ and HCN.

HEAT TRANSFER CHARACTERIZATION

Figures 20 and 21 display the radiation and total flux measurements obtained for various reactor wall temperatures. Wall temperatures were determined by optical pyrometer readings. The argon carrier gas was not preheated in order to minimize gas phase secondary reactions of tars. As Figures 20 and 21 indicate, the main mode of heat transfer to the probe is via radiation at each of the reactor wall temperature settings, the convective flux being determined by the difference between the total and radiative flux readings at a particular position.

In order to estimate particle temperature trajectories, the carrier gas temperature must be determined as a function of reactor position. Two methods were employed to determine gas phase temperatures. One involved calculating the gas temperatures needed to produce the measured convective fluxes to the probe surface. A second method involves making a series of temperature measurements made with thermocouple beads of varying size characteristics. Extrapolation to zero bead size eliminates, in principal, the radiation component of heat transfer, leaving the estimated entrained gas temperature. Table IV lists center position gas temperature estimated in each manner.

RESULTS

Moderate Heat Flux Conditions - Heated Grid Investigation

Low pressure runs were performed to ascertain the effect of coal rank on total volatile yield. Final particle temperatures of approximately 900 C were achieved and held for ten seconds. A range of heating rates were employed, depending on coal type. The tar (polycyclic aromatic species - PAH) yields obtained for subbituminous and Rocky Mt. bituminous coals were observed to be more sensitive to changes in apparent sample heating rate through 900 C than

Appalachian Province high volatile bituminous coals. Figure 22 shows the product distribution trends as a function of carbon content of a coal sample under conditions of maximum tar (condensable PAH) yields for each coal type. Generally, coals of lower aromaticity (see above Sample Characterization discussion) require lower heating rates than Appalachian Province bituminous coals to maximize tar yields. For example, for the bituminous coals with measured carbon contents ranging from 76 - 80%, a heating rate of 500 C/sec to an asymptotic particle temperature of 900 C produces widely varying tar yields (Figure 23), depending on the aromaticity and, therefore, thermal stability of the mix of molecular species in the particular bituminous coal.

In conditions in which pressure-induced, that is, interphase mass transport conditions are minimized, the extra-particle evolution of parent coal nitrogen mirrors the distribution of parent coal mass evolved as tar species. Figures 24a and 24b display plots of mass fraction of parent coal nitrogen as condensable tar species versus the mass fraction of parent coal nitrogen evolved as an heteroatom element in the condensable tar species. Variations in tar yields for a given coal represent ranges of heating conditions.

Figures 25a and 25b indicate the relationship between total volatile yield, indirectly given by the fraction of coal remaining as char, and the fraction of original coal nitrogen remaining in the char. To a mass fraction yield of 0.5, the mass fraction of parent coal nitrogen evolved mirrors the coal volatile yield. Beyond a mass fraction yield of 0.5, the residual char loses nitrogen in a mass fraction ratio disproportionately greater than the total mass loss. These char "degassing" reactions are slow, even at particle temperatures greater than 900 C, relative to the initial 0.5 mass loss. Total nitrogen volatility is not a strong function of coal type for high volatile bituminous coals and lower ranks. For higher rank coals, the nitrogen volatile yield, and its distribution between tars and light gases, primarily HCN, is seen to reflect the devolatilization characteristics of the coal as given in Figure 22.

As tar yields for a particular coal are varied by changes in heating conditions, the distribution of parent coal nitrogen among tar species and light gas species is also varied. Conversely, for a given heating condition, if tar yields are varied by varying the coal type, the distribution of parent coal nitrogen between tar species and light gas species is varied. Figure illustrates the variation in coal nitrogen distribution with coal rank. The lignite rank "missing" nitrogen is primarily NH₃ in these heating conditions.

Tables V and VI display the nitrogen balance data obtained by heating a subbituminous and a high volatile bituminous coal to various final temperatures with varying heating rates and holding for 10 seconds at that heating rate. The similarity in total nitrogen volatile yield with final particle temperatures of 900 C is apparent. The variation in nitrogen evolution behavior lies in its distribution among volatile types, that is, tar and light gas species. Total tar yield and the susceptibility of tar species to thermal cracking reactions varies significantly with coal type. Pyrolysis reactions of tars result in a reduction in tar yield and the release of ring bound nitrogen as cyanide species. Table VII indicates this trend in another manner, for coals ranging in rank from a lignite to anthracite, by comparing changes in tar yields induced by a change in transient heating conditions with the corresponding observed change in cyanide gas yield.

Intense Heating Conditions - Flash Lamp Investigation

It is of interest to determine if the phenomenological trends observed in the moderate heat flux conditions characteristic of the heated grid are maintained in more intense, and more combustor-like, heating conditions. Using a Pittsburgh Seam HVA bituminous coal (PSOC 1451) as a reference, the nitrogen devolatilization behavior was observed in the flash lamp apparatus previously described. This Pittsburgh Seam coal has an elemental composition very similar to the PB sample of Table I. Table VIII a-d displays the product distributions observed for this coal in the range of conditions indicated.

The evolution of parent coal nitrogen from the parent coal particle is initially associated with the evolution of tars. Significant coal nitrogen evolution as cyanide species is observed only after particle or volatilized heavy hydrocarbons are held at temperatures around 800 C or above for extended times. The low cyanide yields in vacuum indicate the main tar evolution occurs at transient temperatures below this value and the rapid devolatilization process ablatively cools the particles. Devolatilizing the same coal under one atmosphere of argon or helium introduces a mass transfer resistance to the escape of heavy hydrocarbons, but at the same time provides a particle cooling mechanism via the particle-ambient gas boundary layer. The order of magnitude greater thermal conductivity of helium relative to argon maintains lower transient particle temperatures (See Table III). The change in transient particle temperatures with heating conditions is reflected in the volatile yields and the distribution of volatile gases. Conditions promoting average particle and particle-gas boundary layer temperatures of 800 C or greater lead to intraparticle and boundary-layer secondary reactions of tars resulting in the evolution of ring bound nitrogen as HCN. Phenomenologically, the production of cyanide species from high temperature reactions of tars and char degassing reactions is also associated with the appearance of CO, C₂H₂ and soot species. Soot species are observed by TEM inspection of the carbon black deposits in the reactor.

Tables IX and IXb indicate the same phenomenological trends observed for a range of coal ranks in moderate heating rate conditions is also observed in transient, high intensity heating of small particles. That is, tar yields are a strong function of coal characteristics and high temperature secondary reactions of tars and residual chars vary significantly with aromaticity of the parent coal. Again, for a given coal type the thermally induced pyrolysis reactions that produce large increases in cyanide species are phenomenologically associated with proportional increases in CO and C₂H₂. Again, for a given coal, TEM inspection of carbon black deposits indicates that soot formation is associated with the presence of C₂H₂ and HCN in the devolatilization gases.

Entrained Flow Reactor Devolatilization

Entrained flow devolatilization involves transient particle heating in intermediate heat flux conditions to that of the the heated grid and flash lamp. As noted above the flow reactor as operated to date in this laboratory involves no preheating of the argon carrier gas. This is done purposely to aid in deconvoluting the tar evolution and secondary reaction processes.

A Pittsburgh Seam #8 coal, 20 - 30 micron size cut, was devolatilized in the flow reactor. A series of runs were made at the various wall temperatures indicated. Ash tracer techniques applied to the CO stage cyclone char was used to measure the total volatile yield obtained for a given wall and estimated gas temperature. Mass fraction yields are shown in Figure 27. Light gas yields, as determined via the multipass gas cell connected to a FT-IR instrument are displayed on a relative basis in Figures 28 through 32. Char and tar elemental and IR absorbance characteristics are shown in Figures 33 through 32 for selected wall temperatures.

The results indicate the same devolatilization process is followed by the high volatile bituminous coal in these heating conditions as is observed in the moderate heating conditions of the heated grid apparatus and the intense heating conditions of the flash lamp. That is, the initial release of fuel bound nitrogen is via high molecular weight hydrocarbons (tars) with some slight release of coal nitrogen as cyanide gas. Particle, particle-gas boundary layer temperatures and free stream gas temperatures of 800 C or greater induce pyrolysis reactions of these heavy hydrocarbons which result in the formation of HCN and phenomenologically associated CO and C₂H₂. Aliphatic and oxygen functionality in the tars decrease. The onset of these high temperature secondary reactions in tars is associated with an increase in the "background" absorption observed in the infrared absorbance spectra of the tars. This increase in background absorption is attributed to the presence of condensed aromatic ring species in the aerosol phase and is due to the onset of soot formation in tar species.

SUMMARY AND CONCLUSIONS

On a mass fraction basis, the nitrogen devolatilization of a coal mirrors the mass fraction devolatilization of the parent coal in moderate heating rate conditions, that is, in heat flux density regimes of 1 - 10 watts/cm². In these conditions, the split of coal nitrogen between tar and light gas species mirrors, to a first order approximation, the distribution of coal mass into tar and light gas species. The distribution of parent coal mass between these species varies significantly with the chemical characteristics of the parent coal, in particular, those indices associated with thermodynamic stability. Since the parent coal nitrogen traces the volatiles distribution pattern both as a function of coal type, given a set of heating conditions, and for a given coal type with varying heating conditions, the parent coal nitrogen behaves as if is uniformly distributed throughout the mix of ring structures present in the parent coal.

Similar phenomenological behavior is indicated in the intense heating conditions associated with flash lamp devolatilization. That is, the distribution of parent coal nitrogen in light gas species and tar species varies significantly with coal type given a set of heating conditions and with heating conditions given a coal type. In both moderate and intense heating conditions, the total nitrogen evolved, in a manner similar to the total mass evolved, is a weak function of coal rank for HVA coals and lower rank. The chemical nature of the nitrogen in the volatiles phase is highly dependent on the coal type.

Devolatilization experiments performed in three different heat flux regimes indicate the nitrogen devolatilization process for a HVA bituminous coal follows a similar sequence in each regime - see Figure 39 - but overall rates and observable product distributions are highly dependent on the conditions of heating. Devolatilization commences with the onset of intraparticle tar formation. Rapid heating to particle temperatures of 500 to 700 C emphasizes the desorption of tar species intact via vaporization, convective entrainment with light gases being formed in the particle, of a non-equilibrium, irradiance enhanced desorption. The mode of tar desorption depends on associated heat and mass transport related parameters, in particular, ambient pressure, nature of the ambient gas and the mode of heat transport to the particle surface (irradiant versus convective). Particle and near-particle gas temperatures of 800 C and above promote the formation of HCN via secondary high temperature reactions of tars. The same reaction network appears to produce CO and C₂H₂ and initiates the onset of gas phase soot formation from secondary reactions of tars.

Variations in nitrogen devolatilization products with coal type can be understood relative to changes in the thermal stability characteristics of the mix of molecular species present in the parent coal. With respect to the rate of light gas NO_x presursors from coal, the overall rate of production is dependent on the intrinsic characteristics of the parent coal coupled to the heat transfer conditions in which the coal is devolatilized. The overall phenomenology of coal nitrogen evolution appears to be outlined and overall rank-dependent parameters are being determined by use of the various reactors noted above.

ACKNOWLEDGEMENTS

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H/C vs. O/C OF COALS AND COAL TAR



Figure 3

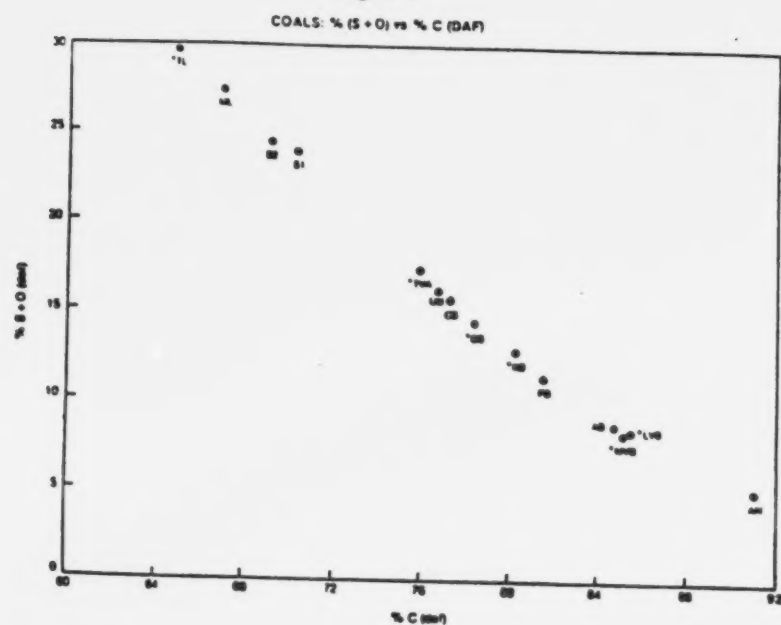


Figure 4

IR ABSORPTION BAND IDENTIFICATION

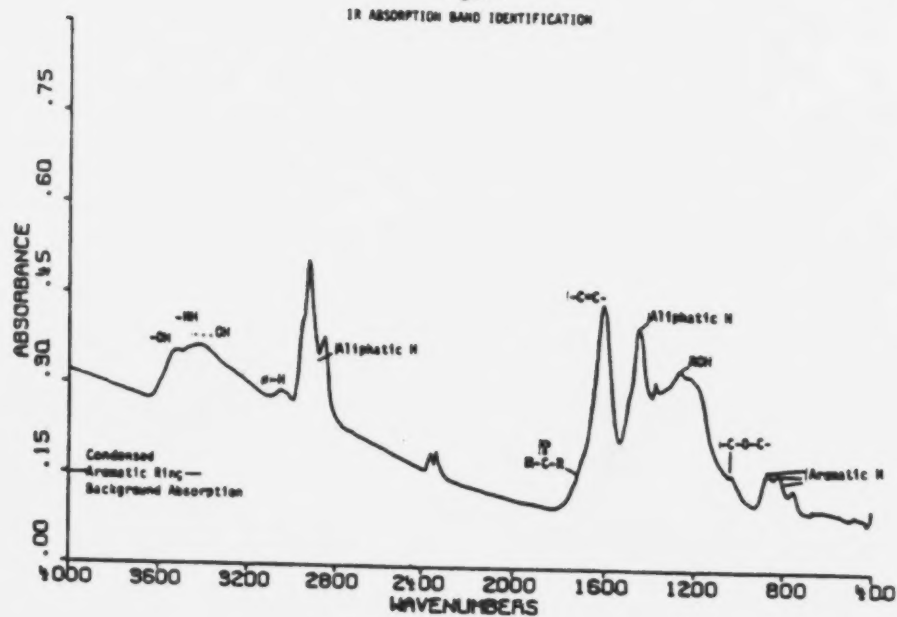


Figure 5
SUBTRACTED BACKGROUND AREA VS % C (Mn)

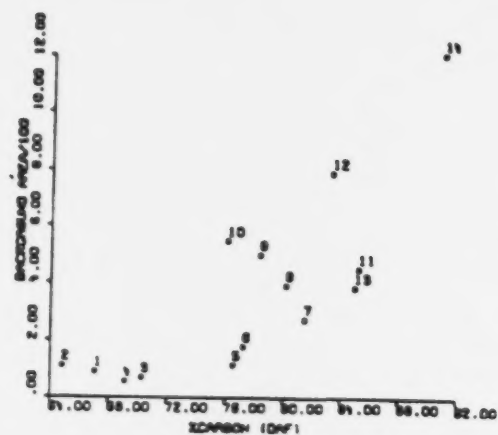


Figure 6
TOTAL ABSORPTION AREA VS % C (Mn)

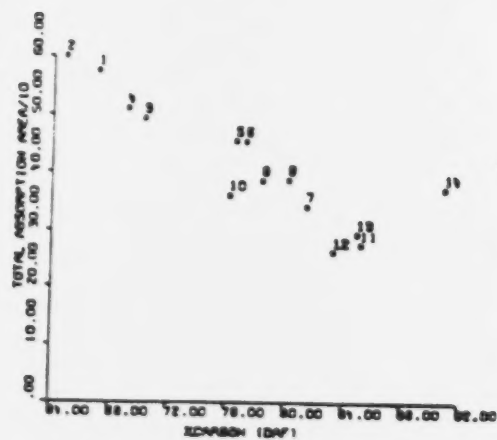


Figure 7
ALIPHATIC H (2760-3000 cm^{-1}) AREA VS % C (daf)

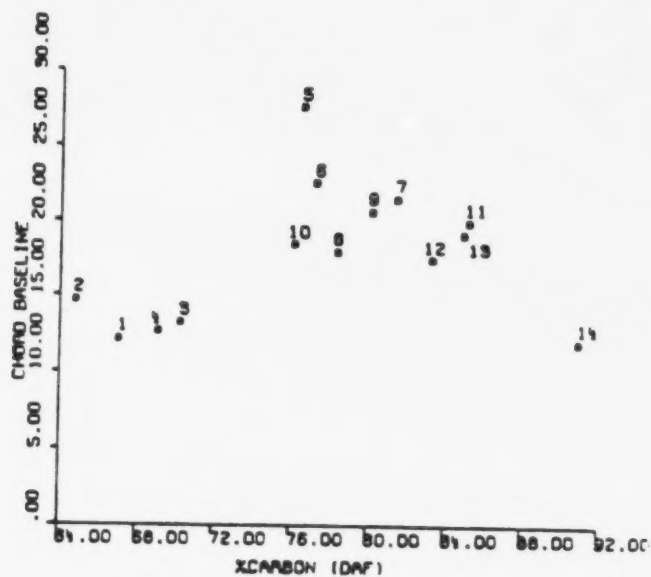


Figure 8
HYDROXYL H (3600-3100 cm^{-1}) AREA VS % C (daf)

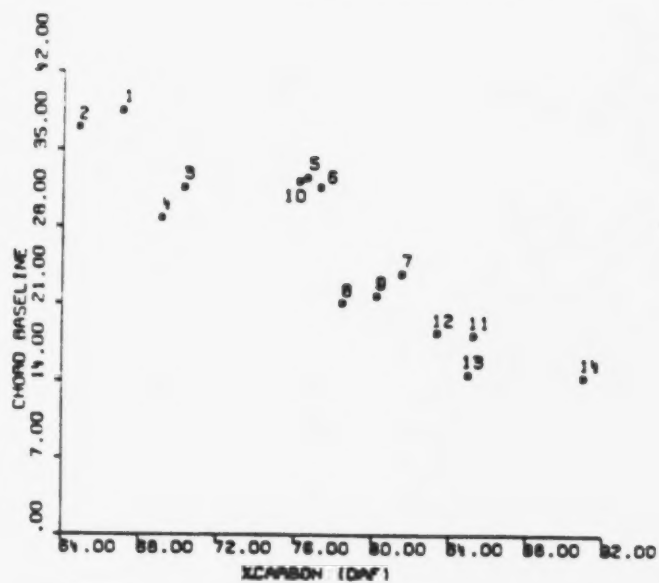


Figure 9

AROMATIC H (680-920 cm^{-1}) AREA VS % C (dal)

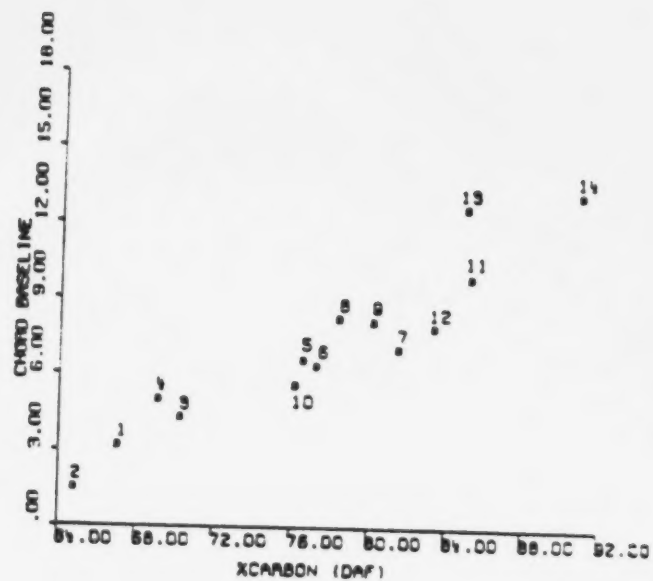


Figure 10

AROMATIC H AREA VS HYDROXYL H AREA

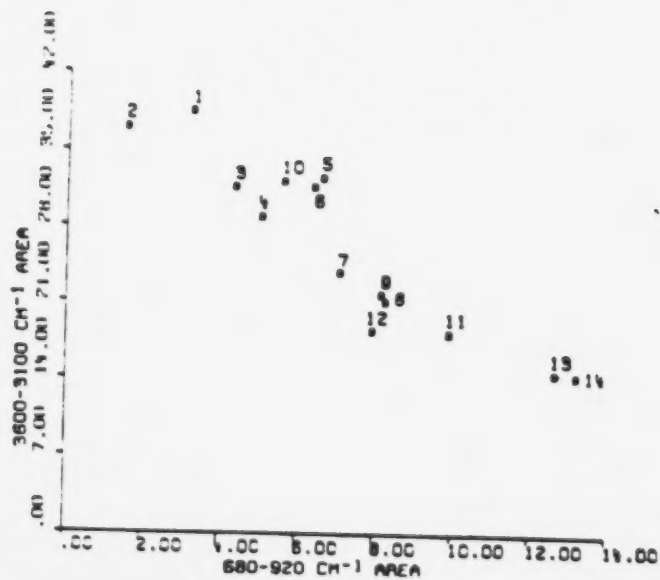


Figure 11a

REACTOR HEAT TRANSFER REGIMES

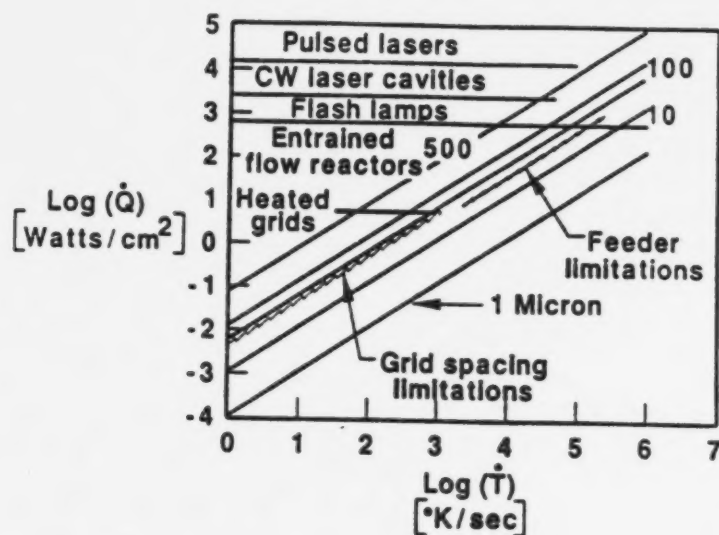


Figure 11b

REACTOR HEAT TRANSFER REGIMES

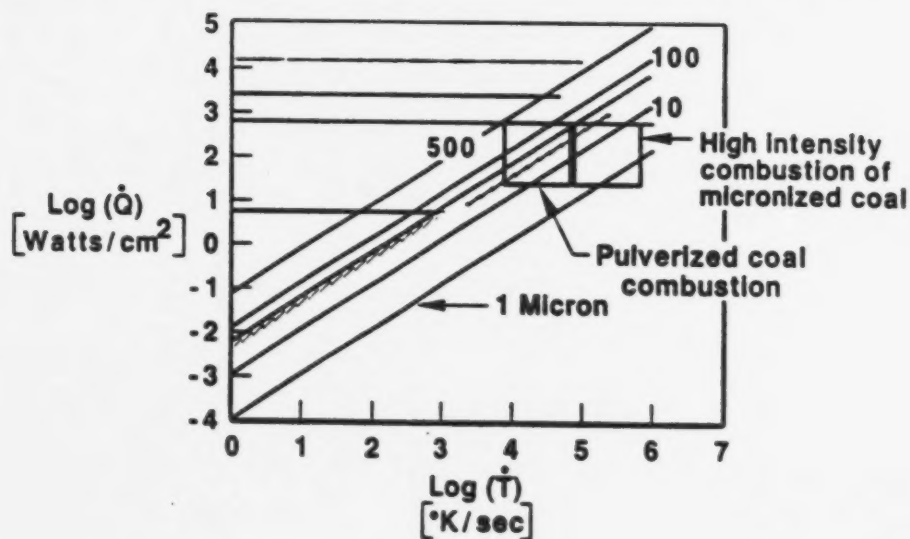


Figure 12

HEATED-GRID DEVOLATILIZATION APPARATUS

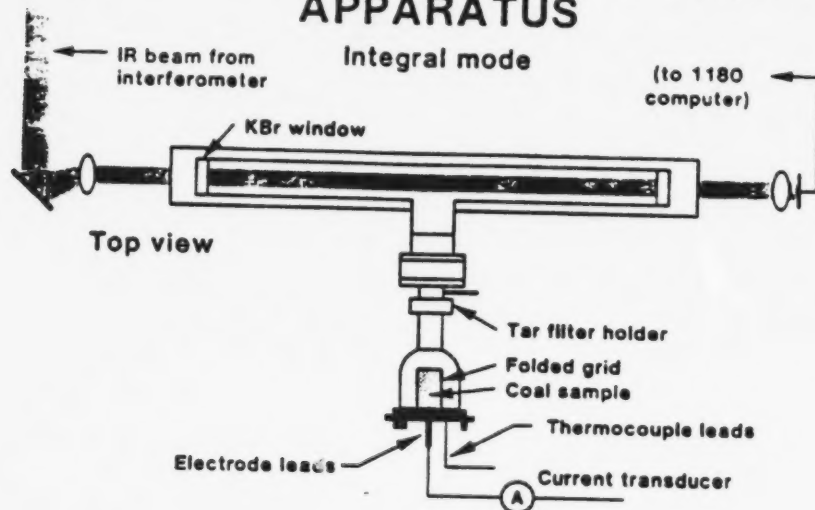
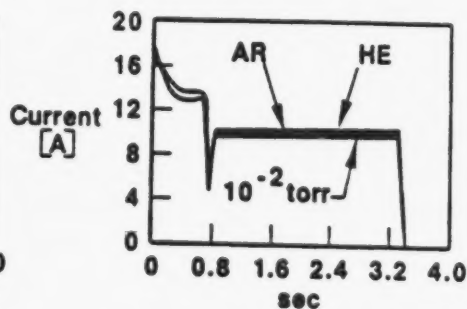
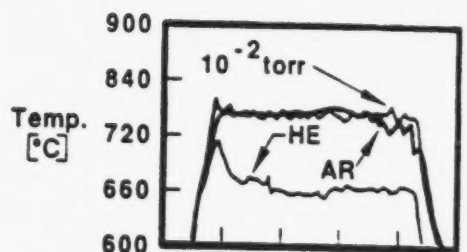
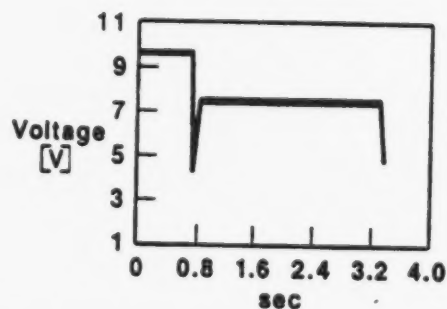


Figure 13

TEMPERATURE, VOLTAGE, CURRENT TRAJECTORIES

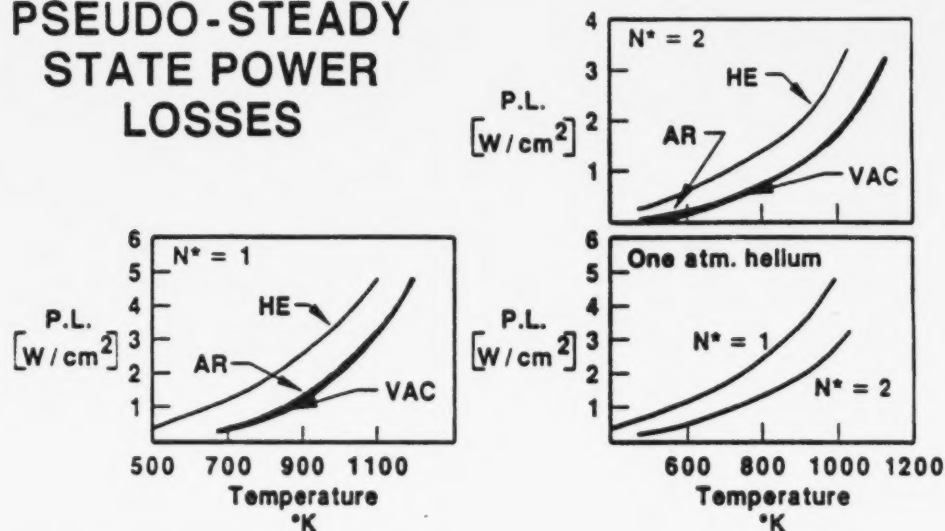
$N^* = 1$ $T_{\text{plateau}, 10^{-2} \text{ torr}} = 780^\circ$



* N = number grid layers

Figure 14

HEATED GRID PSEUDO-STEADY STATE POWER LOSSES



*N = number grid layers

Figure 15a

FLASH REACTOR AND GAS ANALYSIS SYSTEM

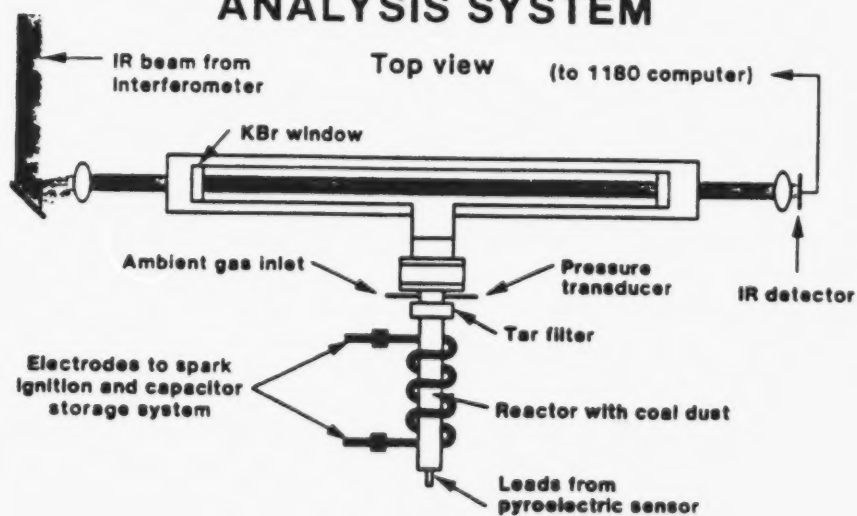


Figure 15b

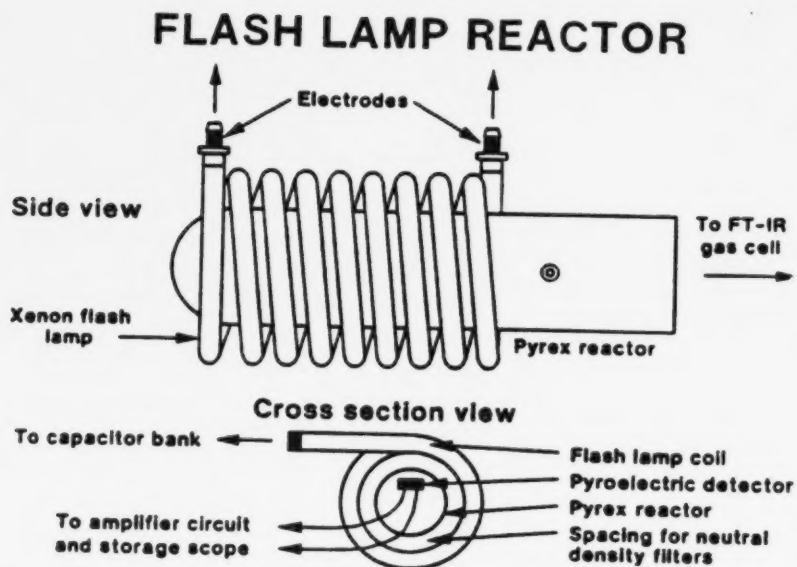


Figure 16

FLASH LAMP PULSE SHAPE

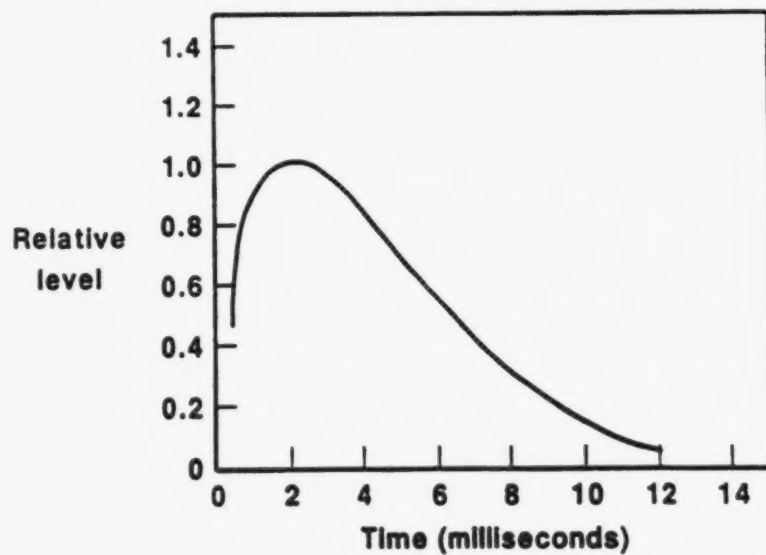


Figure 17

ENTRAINED FLOW REACTOR FOR COAL DEVOLATILIZATION

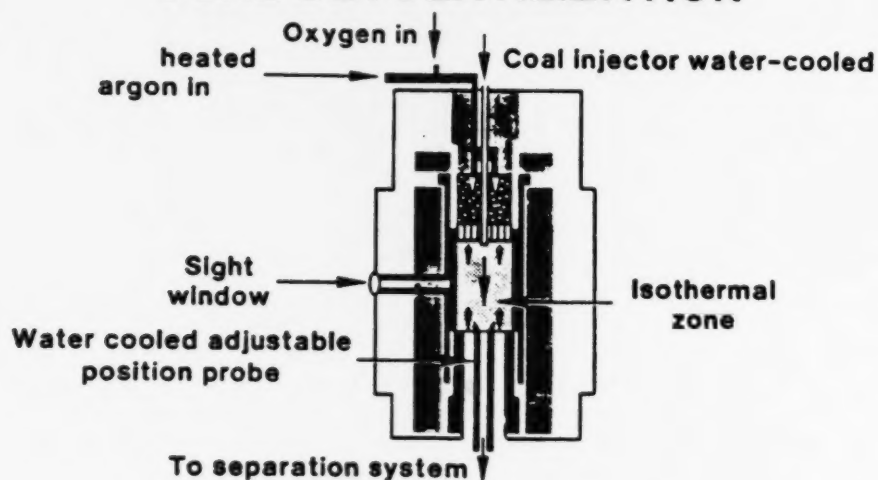
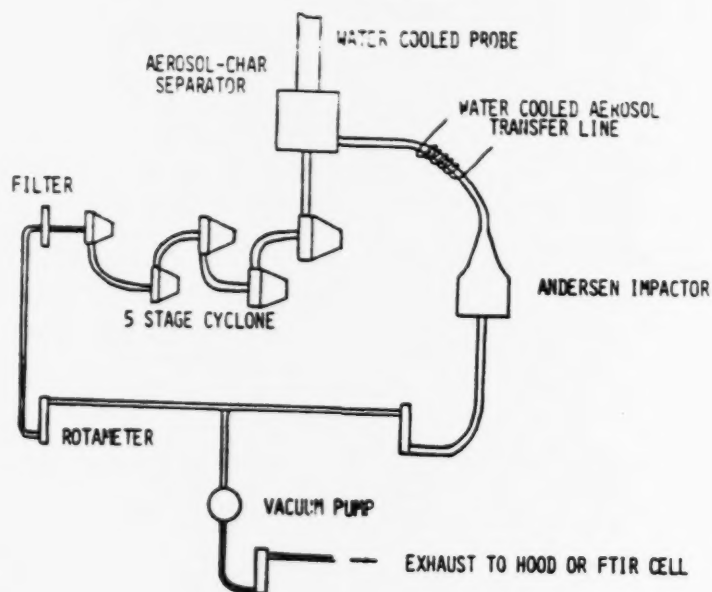


Figure 19



SAMPLE COLLECTION SYSTEM



Figure 18
AEROSOL - CHAR SEPARATION APPARATUS

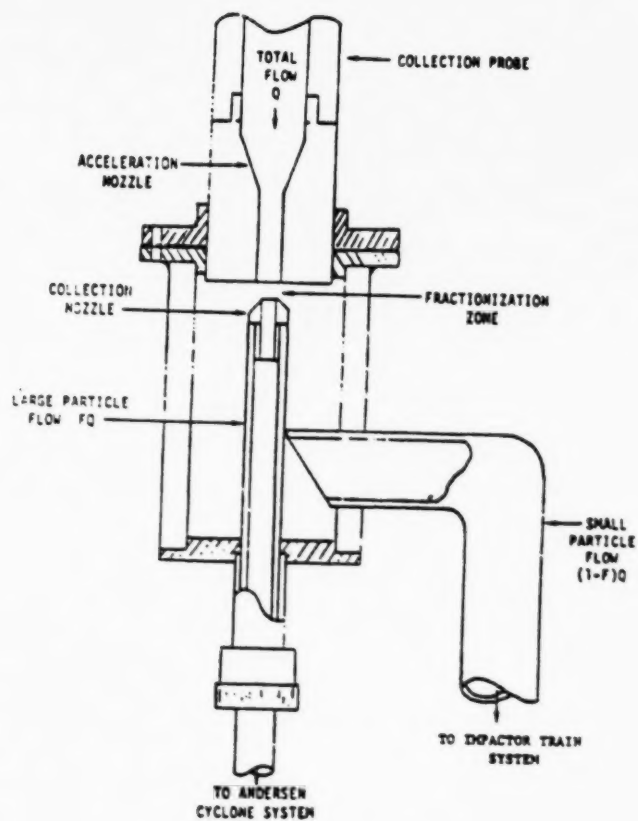


Figure 20
HWHG REACTOR RADIATIVE FLUX PROFILES

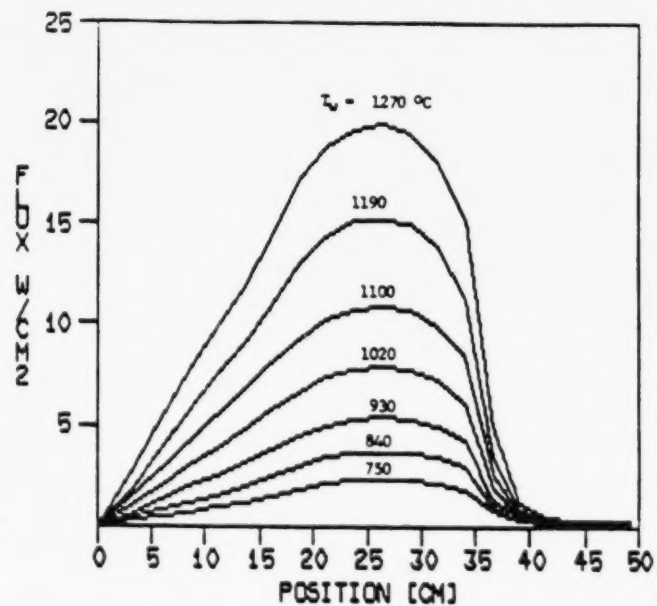


Figure 21
HWHG REACTOR TOTAL FLUX PROFILES

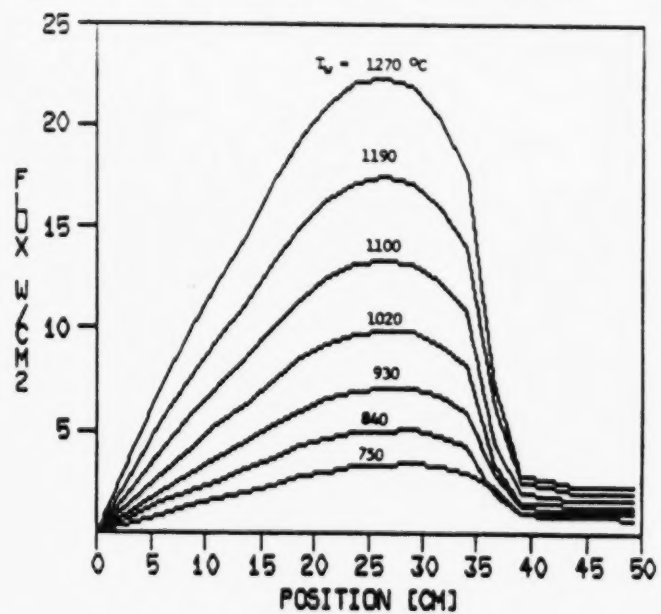


Figure 22

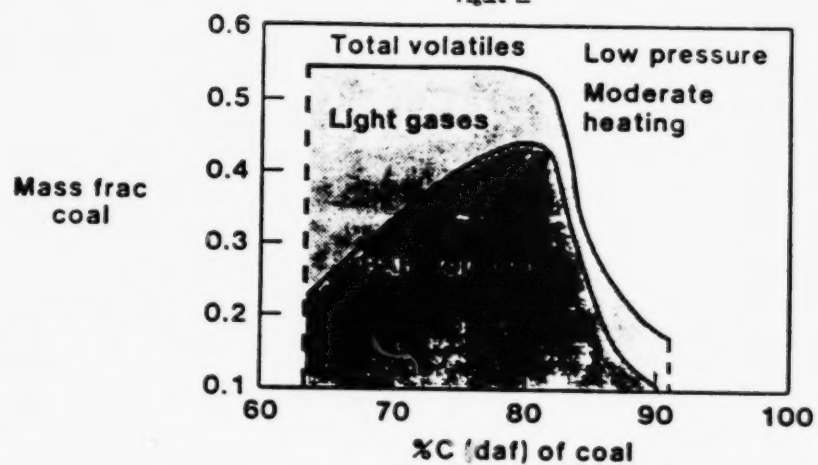
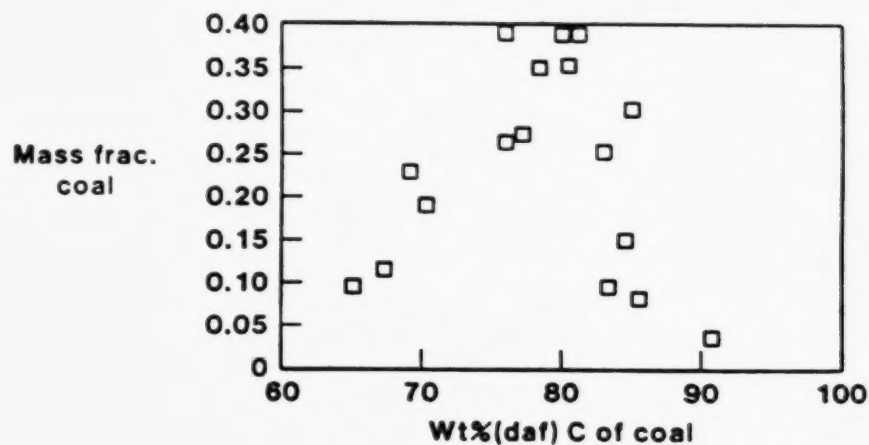


Figure 23

TAR YIELDS vs C% (daf)



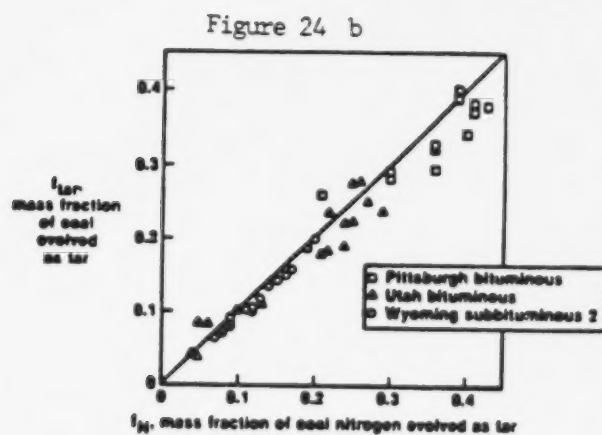
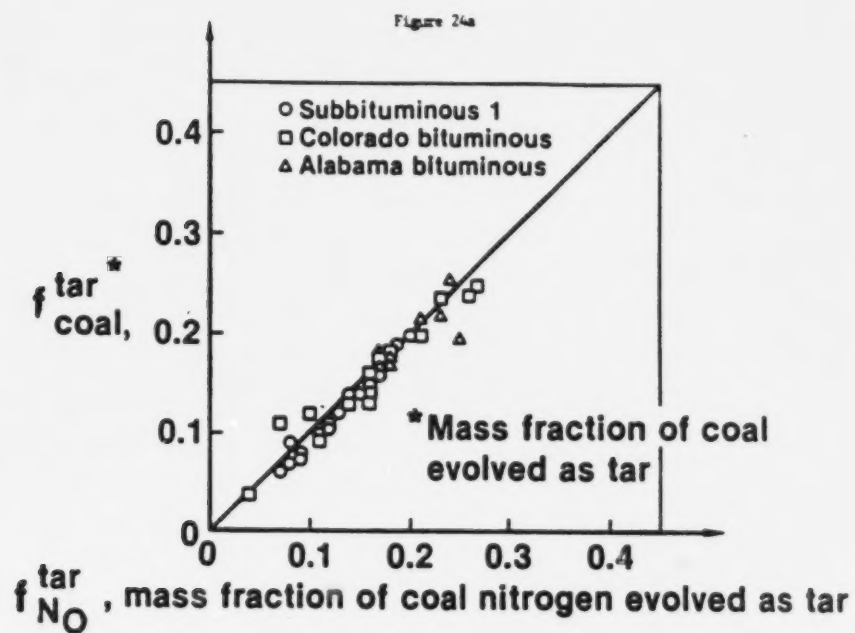


Figure 25a

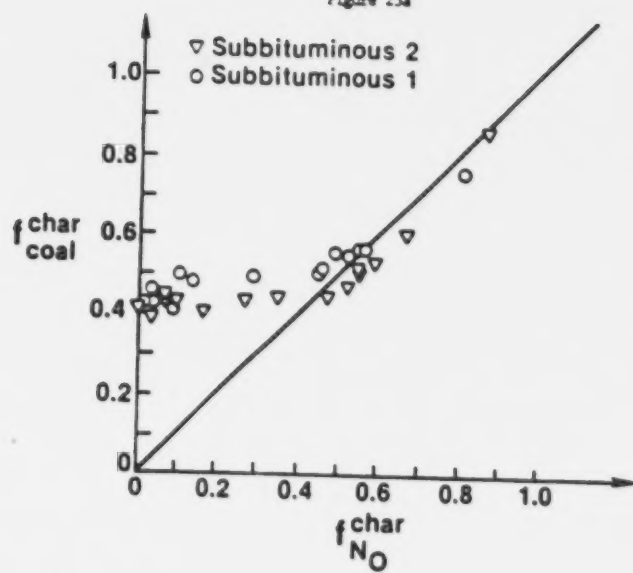


Figure 25b

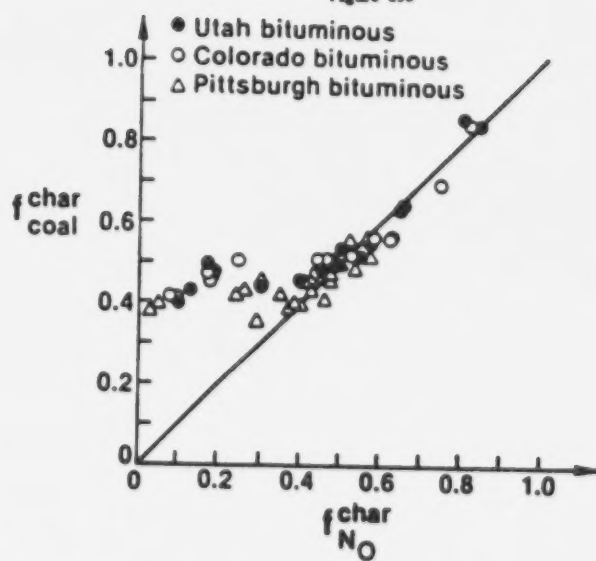


Figure 26

N DISTRIBUTION MODERATE HEATING

Heating rate: 500 K/sec Tot. contact time: 4 sec;
 Final temperature: 1273 K -270 + 325 mesh
 Ambient pressure: 0.001 torr

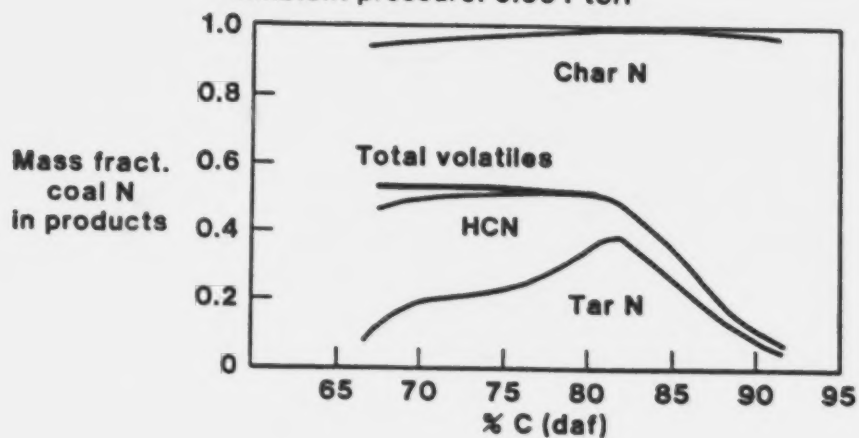


Figure 27

MASS FRACTION YIELD VS. REACTOR WALL TEMPERATURE (°C)
 VORTEC P50C 145: 20-30 MICRONS 600 MSEC

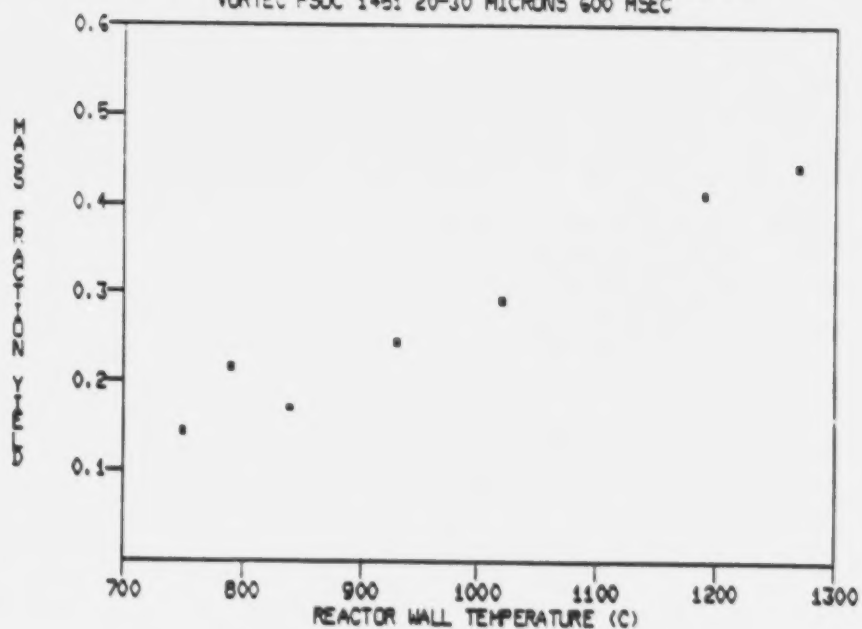


Figure 28
CH₄ VS. REACTOR WALL TEMPERATURE (C)
VORTEC PSOC 1451 20-30 MICRONS 600 MSEC

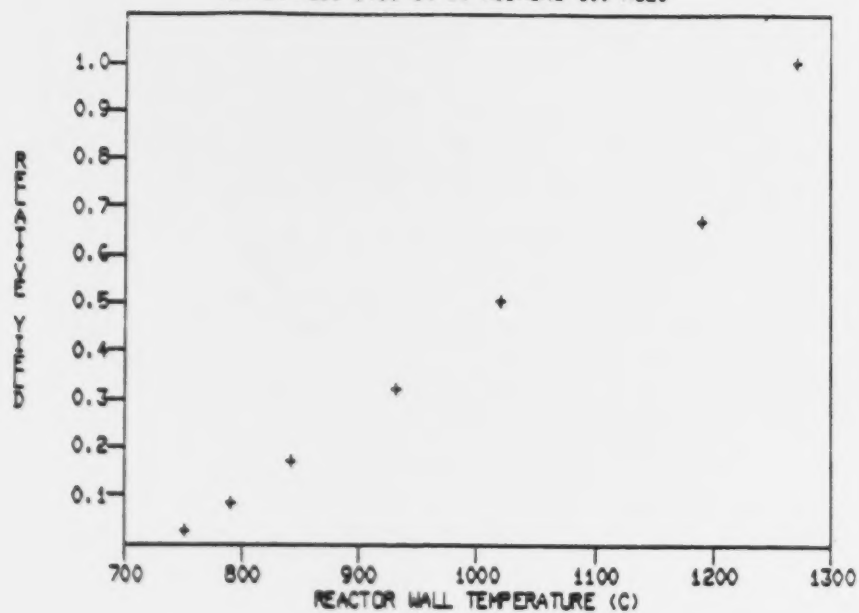


Figure 29
C₂H₄ VS. REACTOR WALL TEMPERATURE (C)
VORTEC PSOC 1451 20-30 MICRONS 600 MSEC

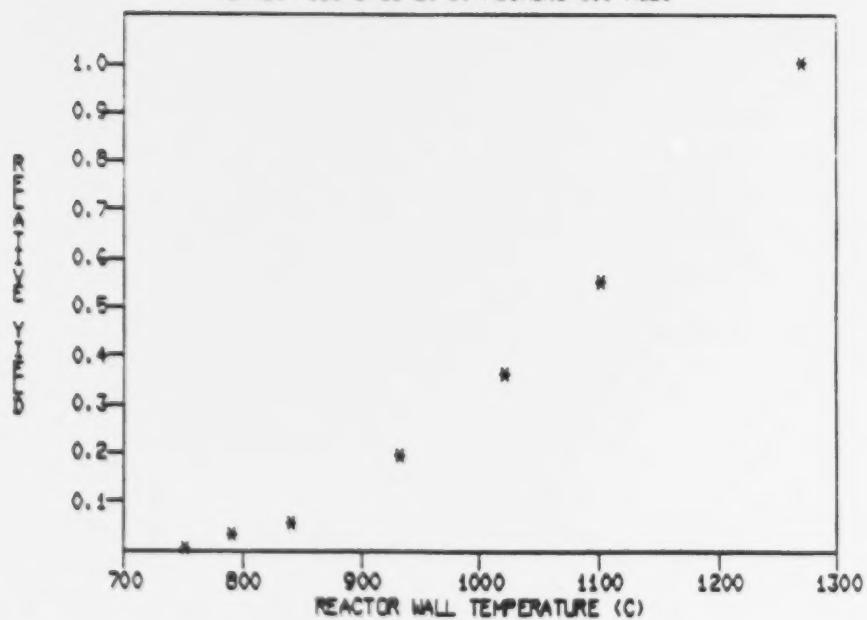


Figure 32

C2H2 VS. WALL TEMPERATURE (C)
VORTEC P50C 1451 20-30 MICRONS 600MSEC

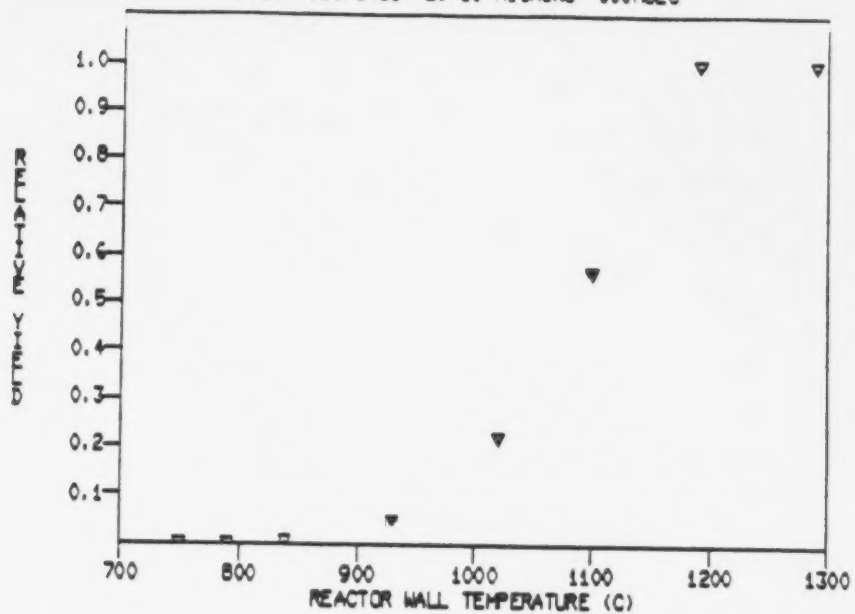
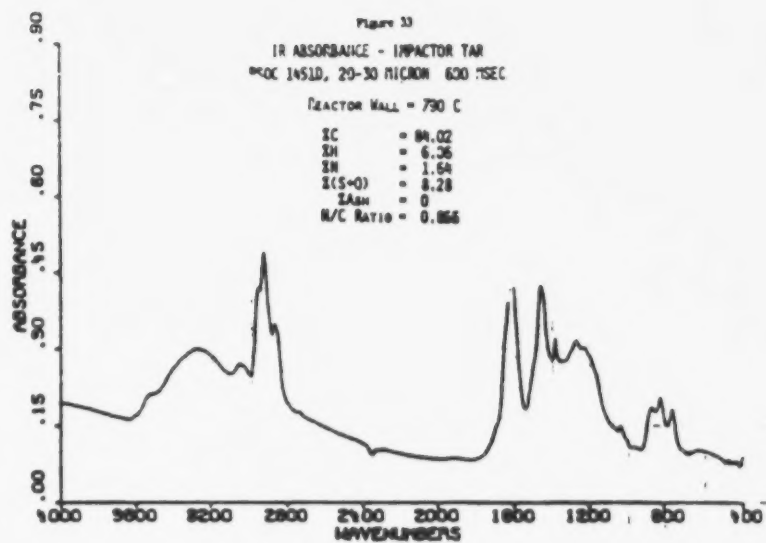


Figure 33

IR ABSORBANCE - IMPACTOR TAR
PDC INSID, 20-30 MICRON 600 TSEC

REACTOR WALL = 730 C

IC = 84.02
IH = 6.36
IN = 1.64
I(S-O) = 8.28
IASH = 0
H/C RATIO = 0.866



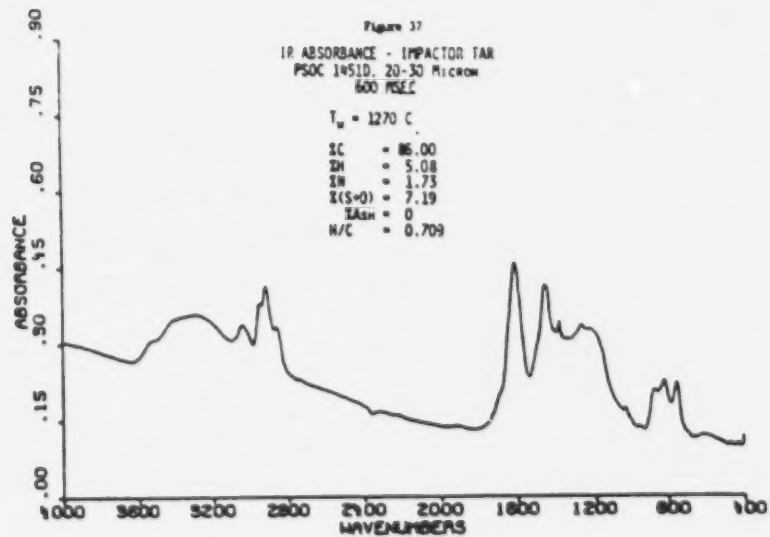
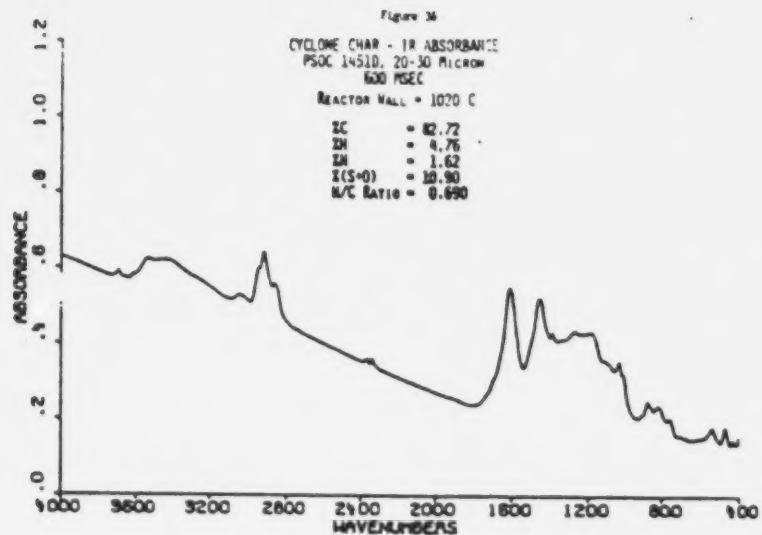


TABLE I

ELEMENTAL COMPOSITION OF COALS

Parent coals*		C	H	N	S+O	H/C	S+O/C
1) Lignite	ML	67.06	4.65	1.00	27.30	0.83	0.30
2) Lignite	TL	64.82	4.82	1.34	29.02	0.89	0.33
3) Sub B	S1	70.26	4.61	1.21	23.92	0.78	0.25
4) Sub B	S2	69.13	5.28	1.54	24.04	0.92	0.26
5) hvB Bit	UB	76.59	5.65	1.66	16.09	0.88	0.16
6) hvB Bit	CB	77.26	5.39	1.73	15.61	1.01	0.15
7) hvA Bit	PB	81.50	5.41	1.54	11.53	0.80	0.11
8) hvA Bit	OB	78.42	5.18	1.92	14.48	0.79	0.14
9) hvA Bit	KB	80.20	5.32	1.63	12.85	0.80	0.12
10) hv - Bit	TVA	76.18	5.11	1.60	17.12	0.83	0.17
11) MV Bit	MVB	85.25	5.00	1.50	6.84	0.70	0.06
12) MV Bit	AB	83.36	4.71	1.70	10.24	0.68	0.09
13) LvB	LVB	84.98	4.61	1.61	8.74	0.65	0.07
14) Anthracite	AN	90.99	3.28	0.86	4.92	0.43	0.04

*DAF Basis

TABLE II

STRUCTURE ASSIGNMENTS IN ABSORPTION SPECTRA
HYDROCARBON STRUCTURES

BAND (CM-1)

ASSIGNMENT OF STRUCTURES

700 - 900	AROMATIC RING N OUT OF PLANE BENDING
3000 - 3100	AROMATIC RING N STRETCHING
2000 - 4000*	CONDENSED AROMATIC RING STRUCTURES
2400 - 3000	ALIPHATIC N STRETCH
2000 - 3620	HYDROXYL AND AMIDE N IN VARYING STATES OF HYDROGEN BONDING

PEAK/SHOULDER (CM-1)

3560	HYDROXYL N IN PHENOL GROUPS
3420	AMIDE BONDED N; PYRROLE RING N
3240	HYDROXYL N IN PHENOL GROUPS WHICH ARE HYDROGEN BONDED TO SALINE MATRIX AND INTRA-MOLECULAR HYDROGEN BONDED
2965, 1385	N CONTAINED IN -CH3 GROUPS
2860, 2930, 1465	N CONTAINED IN -CH2 GROUPS
1140	ETHER OXYGEN
1220, 1270	HYDROXYL N

* BROADBAND BACKGROUND ABSORPTION DUE TO PHOTO PROMOTION OF VALENCE BAND ELECTRONS TO CONDUCTION BANDS OF MOLECULAR ORBITALS ESTABLISHED IN CONDENSED AROMATIC RING STRUCTURES. HYDROXYL N AND AMIDE N ABSORPTION BAND (2000 - 3620 CM-1) "RIDES" ON TOP OF THIS BAND. BACKGROUND ABSORPTION INCREASES WITH EXTENT (NUMBER DENSITY AND SIZE DISTRIBUTION) OF AROMATIC RING CONDENSATION WITHIN A SAMPLE.

TABLE III

CHARACTERISTICS OF DELIVERED FLASH LAMP PULSES

Ambient Conditions	Capacitor Bank Voltage (kV)	SWF	Maximum Delivered [†] Irradiance (w/cm ²)	Time Average ^{**} Particle Temp. (°C)	Averaging Interval (msec)	Maximum Particle Temp. (°C)	Average [†] Heating Rate (C/sec)
Vacuum	1.5 (0.5)††	30	320	336	359.0	977	6.1x10 ⁴
1 atm. Ar	1.5	30	320	492	18.8	855	4.8x10 ⁴
Vacuum	1.8 (0.7)	30	440	996	389.0	1437	1.1x10 ⁵
1 atm. Ar	1.8	30	440	661	23.5	1020	9.7x10 ⁴
1 atm. He	1.8	30	440	330	6.5	417	2.9x10 ⁴
Vacuum	1.5 (1.0)	60	360	619	396.0	1746	1.7x10 ⁵
1 atm. Ar	1.5	60	360	767	25.8	1272	1.3x10 ⁵
1 atm. He	1.5	60	360	395	7.8	512	5.5x10 ⁴
Vacuum	1.5 (1.5)	90	830	668	401.0	2241	2.6x10 ⁵
1 atm. Ar	1.5	90	830	960	28.3	1755	2.2x10 ⁵
1 atm. He	1.5	90	830	508	9.3	687	9.8x10 ⁴
Vacuum	2.2 (2.2)	60	1400	681	405.0	3060	4.4x10 ⁵
1 atm. Ar	2.2	60	1400	960	31.8	1755	4.1x10 ⁵
1 atm. He	2.2	60	1400	721	11.0	1052	2.8x10 ⁵

*See Fig. for time-resolved pulse shape.

**Average from time = 0 to particle temperature at 350°C on cooling part of transient temperature response. See next column for averaging interval in msec.

†Average heating rate calculated from $(T_{\text{particle max}} - 29^\circ\text{C}) / (t_{\text{particle max}} - 0 \text{ sec})$; that is, linear average of transient particle response through maximum.

††Numbers in parentheses represent relative flux delivered.

TABLE IV

MHMG REACTOR GAS TEMPERATURE

24 SLPM ARGON

WALL TEMP. (°C)	GAS TEMPERATURE (°C)	
	2 CALC.	3 EXTRAPOLATED T/C MEAS.
750	320	215
840	365	310
930	440	415
1020	495	530
1100	575	670
1190	575	780
1270	605	-

- Centerline gas temp. at axial location of 26.35 cm.
- Gas temp. calculated from measured convective flux (total flux - radiative flux) and by approximating the flux probe as a flat plate with characteristic length of .41 cm.
- Gas temp. determined from extrapolation of thermocouple measurements of decreasing bead diameter to zero diameter.

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TABLE V

NITROGEN DISTRIBUTIONS IN DEVOLATILIZATION PRODUCTS

Moderate heating rate
Subbituminous 2 (Sub B) (S²)

$\dot{T}$ (C/sec)	T_f (°C)	f_{CHAR}^N	f_{tar}^N	f_{HCN}^N	Σf^N
~ 100	520	0.99	0.05	-	1.04
↓	600	0.76	0.24	0.01	1.01
	745	0.67	0.19	0.10	0.96
	820	0.63	0.28	0.17	1.00
	890	0.57	0.22	0.21	1.00
	945	0.57	0.12	0.20	0.89
	950	0.53	0.11	0.30	0.94
	1040	0.48	0.17	0.30	0.95
	1090	0.40	0.14	0.40	0.94
~ 1000					

TABLE VI

NITROGEN DISTRIBUTIONS IN DEVOLATILIZATION PRODUCTS

Moderate heating rate
Pittsburgh Bituminous (HVA)
(PB)

$\dot{T}$ (C/sec)	T_f (°C)	f_{CHAR}^N	f_{tar}^N	f_{HCN}^N	Σf^N
~ 100	565	0.61	0.49	0.01	1.11
↓	585	0.61	0.38	0.01	1.00
	618	0.58	0.45	0.00	1.03
	735	0.55	0.41	0.05	1.01
	745	0.59	0.41	0.05	1.05
	775	0.52	0.44	0.10	0.94
	830	0.53	0.39	0.06	0.99
	855	0.54	0.43	0.09	1.01
	915	0.46	0.36	0.10	1.07
	935	0.55	0.36	0.10	0.96
~ 1000	1040	0.44	0.40	0.08	1.09

TABLE VII

VARIATION OF HCN YIELD WITH TAR YIELDS MODERATE HEATING RATE CONDITIONS

Coal	%C (DAF)	F-max	ΔF -tar	ΔF -HCN
TL	67.06	0.18	-0.60	+0.45
SB	69.13	0.25	-0.45	+0.50
UB	76.59	0.30	-0.25	+0.30
PB	81.50	0.39	-0.10	+0.05
LVB	84.98	0.25	-0.02	+0.05
AN	90.99	0.05	-	-

F = Mass fraction of parent coal (mass or nitrogen content)

Heating rate varied from 100 k/sec to 500 k/sec

Final temperature = 1273 k; ambient pressure 0.01 torr

4 sec total contact time; 270/325 mesh particles

TABLE VIII-a

VOLATILES RELEASE - PSOC 1451 (HVA BIT) FLASH LAMP APPARATUS 270/325 MESH PARTICLES

Relative flux level: 0.7 (1.8, KV, 30% NDF)

Product	Vacuum	1 ATM. AR	1ATM. HE
CHAR	59	70	90
TAR	31	19	6
CH ₄	0.13	0.16	-
C ₂ H ₄	-	-	-
C ₂ H ₂	-	-	-
C ₆ H ₆	-	-	-
HCN	-	-	-
CO	0.12	0.15	-
CO ₂	0.63	0.12	-

TABLE VIII-b

**VOLATILES RELEASE - PSOC 1451
(HVA BIT) FLASH LAMP APPARATUS
270/325 MESH PARTICLES (Con't)**

Relative flux level: 1.0 (1.5, KV, 30% NDF)

Product	Vacuum	1.0 ATM. AR	1.0 ATM. HE
CHAR	57	59	78
TAR	37	24	12
CH ₄	0.25	0.29	-
C ₂ H ₄	0.09	0.12	-
C ₂ H ₂	-	0.36	-
C ₆ H ₆	-	-	-
HCN	-	0.47	-
CO	0.23	0.69	-
CO ₂	0.28	0.12	-

TABLE VIII-c

**VOLATILES RELEASE - PSOC 1451 (HVA BIT)
FLASH LAMP APPARATUS
270/325 MESH PARTICLES**

Relative flux level: 1.5 (1.5 KV, 90%NDF)

Product	Vacuum	1.0 ATM. AR	1.0 ATM. HE
CHAR	59	63	76
TAR	27	18	19
CH ₄	0.82	0.34	0.25
C ₂ H ₄	0.51	0.09	0.06
C ₂ H ₂	0.79	1.16	1.01
C ₆ H ₆	0.09	-	-
HCN	0.32	0.65	0.41
CO	1.43	3.01	1.77
CO ₂	0.34	-	0.13

TABLE VIII-d

**VOLATILES RELEASE - PSOC 1451 (HVA BIT)
FLASH LAMP APPARATUS
270/325 MESH PARTICLES (Cont.)**

Relative flux level: 2.2 (2.2 KV, 60%)

Product	Vacuum	1 ATM. AR	1 ATM. HE
CHAR	53	67	70
TAR	25	22	17
CH ₄	0.66	0.38	0.75
C ₂ H ₄	0.01	0.14	0.23
C ₂ H ₂	1.41	1.90	1.48
C ₆ H ₆	-	-	0.17
HCN	0.56	1.39	1.11
CO	1.68	5.35	4.44
CO ₂	-	0.25	0.14

TABLE IX-a

DEVOLATILIZATION BEHAVIOR AND COAL RANK
1 atmosphere argon, -15 μ m particles

Coal	Relative flux delivered	Char	Tar	CH ₄	C ₂ H ₆	C ₂ H ₄
TL	1.0	97	2	-	-	-
TL	1.3	86	1	0.27	-	0.16
TL	1.5	88	9	0.21	-	0.11
TL	1.8	81	9	0.16	-	0.15
TL	2.7	64	6	0.46	-	0.27
S2	1.0	93	6	-	-	-
S2	1.3	92	6	0.23	-	-
S2	1.5	86	6	0.22	-	-
S2	1.8	77	5	0.32	-	0.09
S2	2.7	62	5	0.28	-	0.07
PB	1.0	77	23	-	-	-
PB	1.3	73	21	0.07	-	-
PB	1.5	72	26	0.09	-	-
PB	1.8	70	28	0.19	-	-
PB	2.7	69	27	0.22	-	0.07
PB	3.6	76	21	0.21	-	-
LVB	1.0	91	7	-	-	-
LVB	1.3	79	12	-	-	-
LVB	1.5	85	10	0.22	-	0.06
LVB	1.8	83	15	0.28	-	0.08
LVB	2.7	92	6	0.21	-	0.08
AN	1.0	99	-	0.08	-	-
AN	1.8	96	-	0.08	-	-

TABLE IX-b

DEVOLATILIZATION BEHAVIOR AND COAL RANK (Cont.)
 1 atmosphere argon, -15 μ m particles

Coal	Relative flux delivered	C ₂ H ₂	C ₆ H ₆	HCN	CO	CO ₂
TL	1.0	-	-	-	0.58	1.27
TL	1.3	0.30	-	0.08	2.62	2.09
TL	1.5	0.28	-	0.22	4.22	1.76
TL	1.8	0.45	-	0.48	8.84	1.62
TL	2.7	1.34	0.27	1.45	14.60	1.94
S2	1.0	-	-	-	0.48	0.88
S2	1.3	0.28	-	0.13	2.94	1.50
S2	1.5	0.43	-	0.34	5.94	1.28
S2	1.8	0.61	0.08	0.94	11.48	1.57
S2	2.7	1.55	-	2.04	16.95	1.37
PB	1.0	-	-	-	-	0.24
PB	1.3	-	-	-	0.14	0.11
PB	1.5	-	-	-	0.35	0.14
PB	1.8	0.19	-	0.05	0.66	0.17
PB	2.7	0.67	0.07	0.44	4.23	0.44
PB	3.6	1.39	0.16	1.20	6.79	0.43
LVB	1.0	-	-	-	-	0.12
LVB	1.3	-	-	-	0.15	0.15
LVB	1.5	-	-	-	0.23	0.14
LVB	1.8	0.26	-	0.01	1.46	0.17
LVB	2.7	0.76	-	0.33	3.48	0.17
AN	1.0	-	-	-	-	-
AN	1.8	-	-	-	0.30	0.60

FEASIBILITY OF REBURNING FOR CYCLONE BOILER NO_x CONTROL

by

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ABSTRACT

This paper presents the results of an engineering and economic feasibility study of reburning as a potential retrofit NO_x reduction method for coal-fired cyclone boilers. Results indicate that the majority of cyclone boilers are suitable for retrofit from the standpoint of available furnace residence time, a key parameter in applying the technology. Heat transfer analysis for a 200 MW cyclone boiler case study predicts insignificant increases in furnace exit gas temperatures; thus, no convective pass or sootblowing modifications would be required. No technical factors were identified that would preclude retrofit of reburning to most of the cyclone boiler generating capacity. NO_x reductions predicted for 200 MW and 700 MW boilers were 50 and 60%, respectively, without derating. These predictions are based upon the units available furnace residence times. Capital and 10-year levelized busbar power cost estimates ranged from \$15 to \$34 per kW and 1.6 to 4.0 mills per kWh, depending on the reburning fuel selected. A follow-on pilot reburning project on a 6-million Btu/hr cyclone-equipped test furnace is also described.

INTRODUCTION

The Electric Power Research Institute (EPRI) contracted with The Babcock & Wilcox Company (B&W) to perform an engineering feasibility study to assess the practicality of applying reburning technology to reduce NO_x emissions from cyclone-equipped boilers. Based on favorable results from this study, EPRI, the Gas Research Institute (GRI), and B&W are now co-funding a cyclone pilot-scale project to substantiate the feasibility study results and provide the basis for a future commercial demonstration. This paper focuses on the results from the feasibility study, but also provides an outline of the pilot project currently in its initial phases.

There are presently 105 operating cyclone units representing approximately 14% of pre-NSPS coal-fired generating capacity (over 26,000 MW). However, these units contribute approximately 21% of the NO_x emitted by pre-NSPS units since their inherent turbulent, high-temperature combustion process is conducive to NO_x formation. Although the majority of cyclone units are 20 - 30 years of age, utilities plan to operate many of these units for at least an additional 10 - 20 years. Since the majority of these units are located in the potential future acid rain emission control area (Midwest), cyclone boilers may be targeted for retrofit NO_x control.

Cyclone-equipped boilers have a unique configuration which prevents application of standard low NO_x burner technology (combustion occurs within a water-cooled horizontal cylinder attached to the outside of the furnace). Furthermore, other conventional NO_x reduction techniques such as two-stage combustion cannot be applied to the full extent due to associated cyclone operational concerns (cyclone corrosion). Reburning is a promising alternative NO_x reduction approach for cyclone-equipped units. The technology involves injecting a supplemental fuel into the main furnace (above the cyclone region) to produce a secondary combustion zone where a reducing atmosphere exists. These local chemical reducing conditions convert NO_x to molecular nitrogen, thus destroying a portion of the NO_x produced in the primary cyclone combustion zone. Although numerous reburning studies for gas/oil/PC-fired boilers have been performed, it is difficult to extrapolate these results directly to cyclone units due to inherent differences in cyclone boiler design and operation. The characteristics of cyclone units that may affect NO_x reduction, solids deposition, and efficiency of back-end equipment when applying this technology include:

- Higher initial primary NO_x levels (0.8 - 1.8 pounds $\text{NO}_x/10^6$ Btu)
- Lower char/ash carryover to the main furnace due to the cyclone slagging capabilities
- Different convective pass and downstream particulate equipment design due to the lower fly ash loadings

The objective of the feasibility study was to make a preliminary assessment of the applicability of reburning to cyclone units using available information on reburning process design and performance. The study involved the following major elements:

- Survey the cyclone boiler population to determine furnace gas residence times for the various cyclone boiler designs and generating capacities
- Specify reburn design criteria which would be compatible with cyclone design and operation (residence times and stoichiometries)
- Design a reburning system for two representative cyclone boilers and provide NO_x reduction predictions

- Assess cyclone/boiler reliability and operability while operated with a reburn system
- Estimate the range of retrofit capital and operating costs

With the successful conclusion from the feasibility study, a pilot combustion project is currently in progress. The major objectives of this work will be to:

- Validate the feasibility study results and expand on the areas of uncertainty which were identified in the study
- Evaluate the major process parameters, such as reburning zone stoichiometry, residence time, reburning fuel type, and quantity
- Determine effects of reburning on:
 - the degree of slagging and fouling in the upper furnace and convective pass
 - combustion efficiency
 - corrosion potential
- Maximize NO_x reduction while maintaining combustion conditions compatible with design and operation of cyclone-equipped boilers

BACKGROUND

The cyclone furnace consists of a cyclone burner connected to a horizontal water-cooled cylinder called the cyclone barrel (Figure 1). This auxiliary furnace was an attractive alternative providing the ability to burn low grade coals, significantly reducing fly ash in the flue gas, requiring less fuel preparation equipment, and allowing for a reduction in total furnace size. Crushed coal and air are introduced radially through the burner into the cyclone barrel. The larger coal particles are thrust out to the barrel walls where they are captured and burn in the molten slag layer which has formed, while the finer particles burn in suspension. The mineral matter melts, exits the cyclone furnace from a tap at the cyclone throat, and is dropped into a water-filled slag tank. The flue gases and remaining ash leave the cyclone and enter the main furnace.

No commercially demonstrated combustion modifications have significantly reduced NO_x emissions without adversely affecting cyclone operation. Past tests with air staging achieved 15 - 30% reductions, but since no mandatory emission regulations were enforced, all further development was halted (1)(2). In addition, cyclone tube corrosion concerns due to the resulting reducing conditions were not fully addressed because of the short duration of these tests.

The recent emergence of the reburning technology offers a promising alternative to conventional combustion controls. During the early 1980s, Tokyo Electric Power Company (Japan) and Babcock-Hitachi K.K. (BHK) jointly developed a technology known as in-furnace NO_x reduction (IFNR) to reduce NO_x emissions from gas, oil, and pulverized coal-fired furnaces. Babcock & Wilcox is the exclusive licensee of BHK's IFNR process. The technology, a version of the process widely known in the industry as reburning, is based upon extensive laboratory research and has been proven in subsequent pilot and full-scale operation in Japan. BHK has applied IFNR as a retrofit technology to ten Japanese wall-fired units. The retrofit units are gas, oil, and coal-fired ranging from 175 to 700 MW in size. Their pilot and full-scale experience has demonstrated NO_x emission levels shown in Table 1. In the U.S., the

technology has been evaluated for wall-fired configurations at pilot-scale, providing nominally 50% NO_x reductions (3).

TABLE 1. NO_x EMISSIONS WITH IFNR

Fuel	NO _x Level (ppm @ 3% O ₂)
Natural Gas	15 - 40
Fuel Oil	40 - 60
Pulverized Coal	50 - 100

Future Cyclone Application	350 - 700*

* Based on a 50% NO_x reduction from existing cyclone emission levels.

FEASIBILITY STUDY RESULTS AND DISCUSSION

CYCLONE REBURN DESIGN CRITERIA

The reburning process employs multiple combustion zones in the furnace, as shown in Figure 2. The main combustion zone is operated at a reduced stoichiometry and has the majority of the fuel input (75 - 85% heat input). The majority of investigations on gas/oil/PC-fired units have shown that the main combustion zone of the furnace should be operated at a stoichiometry of less than 1.0. This operating criteria is impractical for many cyclone units due to the potential for highly corrosive conditions, since most cyclones burn high-sulfur, high-iron content bituminous coals. To avoid this situation and its potentially catastrophic consequences, the cyclone main combustion zone should be operated at a stoichiometry of no less than 1.1 (2% O₂).

The balance of fuel is input above the cyclones in the reburning zone through "reburning ports." The ports are operated in a similar fashion to a standard wall-fired burner. The furnace reburn zone operates at stoichiometries in the range of 0.85 - 0.95. This stoichiometry range is required for maximum NO_x reductions based on laboratory studies (3). To obtain these furnace stoichiometries while maintaining a 1.1 cyclone stoichiometry, reburn burner stoichiometries must be approximately 0.2 - 0.4.

The balance of the required combustion air -- totaling 15 - 20% excess air -- is introduced through overfire air ports. These ports are designed with adjustable air velocity controls to enable optimization of mixing to achieve fuel burnout before the furnace exit.

Pilot and field-scale studies by BHK and other researchers (3)(4)(5)(6) have defined acceptable limits of residence times for the reburning zone. A 50 - 60% reduction can be achieved at residence times greater than 0.45 second. This value was selected as the lower limit of acceptable reburning gas residence time. To complete combustion, adequate residence time is required between the overfire air ports and furnace exit. Based on experience with staged combustion, a minimum of 0.65 second residence time is required to complete fuel burnout. For purposes of this study, a value of 0.65 second was selected as the minimum gas residence time required above the overfire air ports. Thus, a total of 1.1 seconds is required between the reburn ports and furnace exit.

BOILER DESIGN SURVEY

The cyclone boiler population was surveyed to assess the suitability of these units to retrofit the reburning technology. The population was first categorized according to furnace arrangements (single- and opposed-wall fired units) and generating capacities (40 - 1150 MW). Then specific representative units from each category were selected to perform a more detailed reburning application evaluation. The major criteria utilized to determine if the reburn technology could be successfully applied was the estimated furnace gas residence time. In addition, space availability at the anticipated reburn burners and overfire air locations was examined. Table 2 summarizes the eight categories of cyclone boilers that were evaluated.

TABLE 2. CYCLONE BOILER POPULATION SURVEY

<u>Identification</u>	<u>Furnace Arrangement</u>	<u>Burner Arrangement</u>	<u>MW</u>	<u>Installed</u>
2.1	Single-Wall Fired	2 Cyclones/1 Level	40	1959
2.2	Single-Wall Fired	3 Cyclones/1 Level	100	1960
2.3	Single-Wall Fired	4 Cyclones/2 Levels	150	1965
2.4	Opposed-Wall Fired	4 Cyclones/1 Level	190	1961
2.5	Opposed-Wall Fired	7 Cyclones/1 Level	330	1964
2.6	Opposed-Wall Fired	8 Cyclones/2 Levels	420	1968
2.7	Opposed-Wall Fired	14 Cyclones/2 Levels	700	1963
2.8	Opposed-Wall Fired	23 Cyclones/2 Levels	1150	1969

Original boiler design data were utilized to calculate the furnace gas residence times of the above units since actual unit operating data was unavailable. The process to determine these residence times and evaluate their significance involved a three-fold procedure:

- 1) Predict furnace gas flow patterns via past B&W flow modeling experience to confirm the validity of the plug flow residence time calculation method used.
- 2) Utilize unit design data and previously discussed cyclone reburn design criteria to compare available furnace height with the furnace height necessary to apply reburning (residence time criteria).
- 3) Select two actual units to perform a more detailed engineering/cost analysis.

Furnace Gas Flow Patterns

Predicting furnace gas flow patterns for opposed-wall fired units was done utilizing the results from two past B&W physical flow model test programs (4)(5). No directly pertinent data were available for single-wall fired units. The acrylic models used in the B&W flow tests were 1/70 and 1/32 scale and utilized water seeded with neutral buoyancy plastic particles as the working fluid. Physical observation and photographic views indicate that the furnace flow patterns were relatively uniform above the cyclone combustion zone in both of the opposed-wall fired models (with no noticeable areas of downward recirculation). No unusual furnace gas flow patterns are expected in the reburning zones. Thus, the residence time estimations utilizing plug flow conditions appear adequate.

Furnace Gas Residence Time

For each of the representative units listed in Table 2, calculations were made to determine if sufficient furnace height was available to accommodate the necessary reburning residence times identified earlier. The minimum required residence times in the reburn and overfire air zones (0.45 and 0.65 second, respectively) were utilized. The location of the reburning burners was dictated by physical space limitations. The residence time from the cyclone to the reburn burners ranged between 0.15 to 0.30 second. Locating the reburn burners in close proximity to the cyclones should not inhibit the reburning performance since the majority of combustion does occur within the cyclone barrel.

Comparing the actual residence time available in the various units to the minimum required time, a difference between actual boiler furnace height versus necessary reburning boiler furnace height was determined. Thus, for screening purposes, this technique determined if the majority of cyclone units could apply the reburn technology based upon actual available furnace height. Table 3 summarizes these furnace height calculations for the eight units identified in Table 2. The base design specifications utilized to generate this table include:

Fuel Split Between Cyclone and Reburn Zone	80/20
Reburning Fuel	Natural Gas
Cyclone Stoichiometry	1.1
Reburn In-Line Stoichiometry	0.2
Reburn Zone Residence Time	0.45 second
Overfire Air Zone Residence Time	0.65 second

TABLE 3. REQUIRED FURNACE HEIGHT

Unit Identification →	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8
Total Number of Cyclones	2	3	4	4	7	8	14	23
Furnace Width (ft)	18	34	36	26	45	36	60	96
Furnace Depth (ft)	10	16	24	20	24	27	33	33
Elevation of Furnace Exit (ft)	609	703	106	115	305	159	528	541
Required Elevation of Furnace Exit (ft)	626.7	702.3	99.4	124.5	294.0	150.2	505.6	527.7
Difference Between Actual and Calculated Furnace Exit (ft)	17.7	-0.7	-6.6	9.5	-11.0	-8.8	-22.4	-13.3
% Increase in Furnace Zone Height Required	52.1%	-1.6%	-13.4%	12.7%	-15.7%	-9.5%	-23.1%	-14.5%

The difference between the actual (available full load residence time) and calculated (required reburn system residence time) furnace exit elevation is a key factor in determining whether the technology can be applied. In other words, a positive value signifies that additional furnace height is necessary; a negative value indicates sufficient height is available.

Overall, the majority of cyclone units examined showed that sufficient furnace height (available gas residence time) exists to accommodate reburning. The only units which appear unsuitable are the small, single-wall fired boilers (less than 80 MW). Unit 2.1 in Table 3 typifies this category of units where an additional

furnace height of 17.7 feet would be required. This corresponds to increasing the furnace height by over 50%, which is impractical. These units represent less than approximately 7% of the cyclone generating capacity.

Unit 2.4 also requires an additional 9.5 feet, but this corresponds to an increase of only 12.7%. The reburning technology could still be applied to this unit if a reduction in residence times within the main, reburn, and overfire air zones were incorporated. This would, however, lead to a lower expected NO_x reduction.

RETROFIT REBURNING CASE STUDIES

Two boilers -- Unit 2.4 (200 MW) and Unit 2.7 (700 MW) -- were chosen to perform a more detailed technical and economical analysis. Unit 2.4 was selected because, although it is considered to be an acceptable candidate for the technology, non-ideal residence times exist and, therefore, represents a worst case scenario. Unit 2.7 is indicative of the majority of the units reviewed since sufficient residence time to apply the technology was determined. The specific criteria which were varied to evaluate the best conditions available within these units to obtain maximum NO_x reduction includes:

Fuel Split	75/25, 80/20, and 85/15
Reburn Fuel	Gas/Oil/Coal
Reburn (In-Line) Stoichiometry	0.0-0.4 second
Reburn Residence Time	0.45-0.6 second
Overfire Air Residence Time	0.65-0.9 second

Calculations show that under any condition, the 200 MW unit possesses less furnace height than would be optimal to obtain maximum NO_x reduction. The required residence times could be achieved at about 85% of rated full load, but since a derate condition usually is unacceptable, NO_x emissions were predicted at both full and partial loads.

The 700 MW unit has about 22 feet additional furnace height that can be utilized to increase the reburn system residence times. Thus, the optimal design conditions were determined to be the following: 0.60 and 0.85 second for the reburn and overfire air residence times, respectively, and 80/20 main/reburn fuel split.

NO_x PREDICTIONS

At full-load conditions, NO_x reduction predictions for the two reburning applications were 49% and 62% for the 200 MW and 700 MW units, respectively. A 15% derate of the 200 MW facility would provide sufficient residence time within its furnace to achieve a predicted 63% NO_x reduction from full-load baseline conditions. The following summarizes the prediction methodology:

200 MW Unit

Full-load baseline	985 ppm NO @ 3% O ₂ (1.34 lb NO/MKB)
% reduction due to reduced cyclone input	15.7%
Reduced input cyclone baseline	830 ppm NO @ 3% O ₂ (1.13 lb NO/MKB)
% reduction by reburning process	40% (reduced residence times)
Full-load operation, overall NO _x emissions	498 ppm NO @ 3% O ₂ (0.68 lb NO/MKB)
Full-load operation, % overall NO _x reduction	49%
15% derate baseline	870 ppm NO @ 3% O ₂ (1.18 lb NO/MKB)
% reduction due to reduced cyclone input	16%
Reduced input cyclone baseline	730 ppm NO @ 3% O ₂ (1.0 lb NO/MKB)
% reduction by reburning process	50% (full residence times)
85% load operation, overall NO _x emissions	365 ppm NO @ 3% O ₂ (0.50 lb NO/MKB)
85% load operation, overall NO _x reduction	58%
85% load operation, overall NO _x reduction from full load	63%

700 MW Unit

Full-load baseline	1180 ppm NO @ 3% O ₂
% reduction due to reduced cyclone input	23.7%
Reduced input cyclone baseline	900 ppm NO @ 3% O ₂
% reduction by reburning process	50% (full residence times)
Full-load operation, overall NO _x emissions	450 ppm NO @ 3% O ₂
Full-load operation, % overall NO _x reduction	62%

The baseline NO_x predictions were made utilizing B&W design standards for cyclone boilers that^x are based on NO_x emission field data. The NO_x reduction capabilities of a reburning system were^x determined from data available^x from Babcock-Hitachi and other researchers (3)(4)(5)(6). Since no reburning pilot data simulating cyclone characteristics were available, this study assumed that the above referenced research was applicable to approximate NO_x reductions in cyclone boilers.

The NO_x reduction comes from two sources:

- 1) Beginning with a baseline NO_x emission for full-load fuel input to the cyclones, an initial NO_x reduction is realized by diverting fuel to the reburn ports, therefore reducing total heat input (and NO_x) at the cyclones. This initial NO_x reduction ranges from 15 to 25%, depending on the reduced input to the cyclones and the full-load cyclone heat input.
- 2) Tests performed with relatively high primary NO_x levels (>500 ppm) show that approximately 50 - 60% reduction can be achieved regardless of reburning fuel type (gas, oil, coal). Additionally, reburning zone stoichiometries of 0.85 - 0.95 show 35 - 60% reduction capabilities. In the case where reburn residence times are restricted, the overall NO_x reduction by reburning is substantially decreased.

Utilizing this information, the reduction of NO_x emissions by the application of reburning to cyclones is a combined effect of the reburning process and lower heat input to the cyclones. Overall, approximately 20% reduction is realized by decreased heat input, and approximately 50% reduction (in NO_x from the cyclones) can be realized by reburning. The combined effect provides conservatively a 60 to 65% reduction from baseline NO_x emissions, if required residence times are available, and approximately 45 - 50% reduction if residence times are slightly reduced.

OPERATIONAL IMPACTS

The 200 MW case study was utilized to perform a more detailed operational assessment of applying the reburning technology. Following a conceptual design of the reburn system (based on the stoichiometries and residence times determined earlier), the boiler performance and power plant impacts were addressed.

Standard heat transfer calculations were utilized to determine the effect of reburning on furnace absorption, furnace exit gas temperatures (FEGT), and unit efficiency. Since the unit's performance depends on the FEGT, a base-case FEGT for normal cyclone operating condition was determined. The maximum increase of FEGT when applying various reburning combustion schemes (varying fuel type and furnace locations where combustion actually occurs) was 56°F. This increase is considered insignificant such that the unit's efficiency and existing metals in the convective pass should not be adversely affected.

The major uncertainties which are indeterminable at this time are the slagging/fouling potential, unburned combustible losses, and corrosion potential. These items must be addressed during the pilot-scale evaluations.

Present cyclone operation does not require precise control over air and fuel splits. For a given load, fuel and air are divided near-equally between the in-service cyclones, with some cooling air provided to out-of-service cyclones. For successful application of the reburning technology, more precise air and fuel control is required. Secondary air monitors for each cyclone and gravimetric feeders are recommended to assure a balanced air and fuel distribution to each cyclone.

With the reburning technology, the cyclone itself would be operated in a normal manner at all times: startup, shutdown, emergencies, etc. When operating in a low NO_x mode (reburning), the cyclone operates with reduced fuel input and reduced air levels. The addition of reburning equipment should not impact the operational range of the cyclone.

The reburn ports are operated much like a wall-fired burner. The equipment associated with the port includes a lighter/ignitor system and flame detection devices. This equipment is conventional and utilized throughout the industry.

BHK experience with reburning on oil and gas-fired utility boilers has not identified any measurable changes in particulate matter compared to normal combustion. Utilizing coal as the reburn fuel could potentially double the particulate loadings and thus adversely affect the precipitator/baghouse performance. In addition, possible changes in particle size distribution and flue gas properties will need to be addressed. These issues will be site-specific and will be determined on a retrofit-to-retrofit basis.

ECONOMICS

Cost analyses were performed on Unit 2.4 (200 MW) in order to assess the associated total capital and levelized revenue requirements for retrofitting and operating a reburning system. Costs associated with this process include:

- Acquisition and handling of the reburning fuels
- Installation and operation of the reburn system
- Boiler impacts and countermeasures

Table 4 summarizes the economic evaluation per each type of reburning fuel. The following listing summarizes the major equipment components utilized for each reburn fuel:

Major Reburning Control System Components --

All Reburn Fuels

- Reburn Burners
- Overfire Air (OFA) Ports
- Tube Wall Openings/Replacement Wall Panels
- Piping/Ductwork to Reburn Burners/OFA Ports
- Burner/Combustion Control System
- Cyclone Gravimetric Feeders
- Cyclone Secondary Air Monitors

Coal Reburning

- Pulverizer/Gravimetric Feeder
- Bucket Elevator
- Coal Silo
- Structural Steel/Pulverizer Enclosure
- Furnace Corrosion Protection

Oil Reburning

- Positive Displacement Pumps
- Oil Storage Tanks

Gas Reburning

- Assumed \$3 Million Gas Pipeline (if no pipeline exists and a 10-mile long gas line is necessary)
- Gas Substation

TABLE 4. ECONOMIC EVALUATION FOR APPLYING REBURNING TO CYCLONE BOILERS*

Reburning Fuel	Fuel Cost (\$/10 ⁶ Btu)	Main/Reburn Fuel Split	Total Estimated Capital Cost Required (\$/kW)	10-Year Levelized Busbar Power Cost (mills/kWh)
Gas	2.0	80/20	15.2	1.6
	3.0	80/20	15.4	3.7
	2.0	80/20	44.4**	2.5**
	3.0	80/20	44.6**	4.9**
Oil	3.0	80/20	22.3	4.0
	4.0	80/20	22.5	6.4
Coal (Same as main fuel)	1.7	80/20	34.0	1.8

* Based on 200 MW unit operating at 70% capacity with 50% reduction. Cyclone burner operates air-rich (1.1 stoichiometry) and reburn zone fuel-rich (0.9 stoichiometry).

** Assumes \$3 million gas pipeline cost.

Capital costs and 10-year levelized busbar power costs were sensitive to fuel type and cost. Approximately 70 - 90% of the associated 10-year levelized cost is attributed to the fuel cost. Fluctuations in gas and oil costs will affect the attractiveness of utilizing gas and oil as reburn fuels. Fluctuations in gas and oil costs of \$2.0 - \$3.0/10⁶ Btu and \$3.0 - \$4.0/10⁶ Btu, respectively, were evaluated. In addition, for natural gas an assumed gas pipeline cost of \$0 (gas on-site) and \$3 million (10-mile long pipeline) was evaluated, depending on local gas availability.

Assuming the ideal least-cost scenario for each reburn fuel, capital costs range from \$15.2/kW to \$34/kW, and the 10-year levelized busbar power costs range from 1.6 to 4.0 mills/kWh. Gas is a more attractive alternative when evaluating initial capital expenditures (if no gas pipeline cost is included) and is comparable to coal on a 10-year levelized basis when the fuel cost differentials are minimal. The results in Table 4 show the magnitude of fluctuation when the various parameters are altered. If a gas pipeline is necessary (assume 10 miles), the capital cost for this option becomes the highest at \$44/kW. Oil would then be the most cost-effective alternative at \$22/kW. The 10-year levelized costs vary directly with the fuel cost. Utilizing coal as the reburn fuel (assuming it is the same as the main cyclone coal), a constant 1.8 mills/kWh was determined since no additional fuel

costs would be incurred. Gas and oil fluctuate between 1.6 - 4.9 mills/kWh (\$2 - \$3/10⁶ Btu fuel cost) and 4.0 - 6.4 mills/kWh (\$3 - \$4/10⁶ Btu fuel cost), respectively. The cyclone pilot-scale project is essential to clarify the potential of the three reburn fuels.

PILOT REBURN TEST PROGRAM

RESEARCH FACILITY

B&W's 6-million Btu/hr Small Boiler Simulator (SBS) is being utilized to perform the pilot-scale cyclone reburning tests (Figure 3). The SBS is fired by a single, scaled-down version of B&W's cyclone furnace burner. Coarse pulverized coal (44% through 200 mesh), carried by primary air, enters tangentially into the burner. (Pulverized coal had to be used in the SBS instead of crushed coal to obtain complete combustion in this small cyclone.) The combustion air, heated externally to 700° - 900°F, also enters tangentially into the cyclone furnace. The larger coal particles are captured and burn in the molten slag layer formed within the cyclone furnace, while the finer particles burn in suspension. The mineral matter melts, exits the cyclone furnace from the tap at the cyclone throat, and is dropped into a water-filled slag tank. Only 15 - 20% of the ash leaves the cyclone with the flue gases and enters the furnace.

The furnace is water-cooled and simulates the geometry of B&W's front-wall fired cyclone boilers. It consists of four separate water-cooled sections. The lower part of the furnace can be converted to a pulverized-coal firing scheme. Therefore, investigation on both pulverized-coal and cyclone-fired units is possible with the facility. The SBS facility has been operating for a total of 5 years, with the last 2 years being operated in the cyclone configuration. This cyclone facility has been proven to simulate typical full-scale cyclone units via furnace/convective pass gas temperature profiles and residence times, NO_x levels, cyclone slagging potential, ash retention within cyclone slag, unburned carbon, and fly ash particle size. A summary of these comparisons is shown in Table 5.

TABLE 5. COMPARISON OF SBS FACILITY AND FIELD UNITS

	<u>SBS</u>	<u>Field</u>
Cyclone Temperature	>3000°F	>3000°F
Residence Time	1.8 sec at full load	0.7 - 2 sec
Furnace Exit Gas Temperature	2250°F	2200° - 2350°F
NO _x Level	900 - 1200 ppm	600 - 1400 ppm
Ash Retention	80%	60 - 80%
Unburned Carbon	2% in ash	1 - 20%
Ash Particle Size (MMD; Bahco)	6 - 8 microns	6 - 11 microns

The inside surface of the furnace is insulated to yield a furnace exit gas temperature (FEGT) of 2250°F at the design heat input rate of 6-million Btu/hr. A water-cooled tube bank simulates the flue gas time/temperature history inherent in full-scale cyclone convective passes. The tube bank consists of four separate sections for simulating a secondary superheater, reheater, primary superheater, and economizer. Each section consists of a water-cooled jacket and tubes to quench the flue gases. All four sections are connected to a common atmospheric drum. This use of convective tubes to cool the gas, in conjunction with the cyclone furnace, makes this a one-of-a-kind facility among pilot-scale combustors.

The tube bank simulator is equipped with sootblowers and observation ports. These ports are located at the entrance to the secondary superheater, reheater, and primary superheater. In-furnace probing can be performed from these ports for temperature, as well as gas and solid sampling.

Two air-cooled probes are used in deposition tests to simulate the tubes in the convective pass -- one for the secondary superheater and one for the reheater. The probes can be inserted in front of the simulated secondary superheater and reheater sections, respectively. These probes are equipped with thermocouples for measuring temperatures of the wall and inlet/outlet cooling air. The probe wall temperatures are set equal to typical field units' tube temperatures. The heat flux can be obtained from an energy balance on each air-cooled probe. In addition, a commercial sootblower in front of each probe can be used to determine the sootblower pressure required to remove the deposits.

TEST PLAN

The technical objectives of this study are to demonstrate NO_x reductions of nominally 50 - 60% while maintaining acceptable cyclone/boiler operating conditions. Three reburning fuels will be evaluated while operating under various full-scale simulated reburning conditions. Table 6 summarizes the various ranges of reburning criteria which will be evaluated for NO_x reduction capability. Main cyclone/reburn port fuel splits, furnace stoichiometries, and furnace residence times will be varied. Additional variables which will be evaluated include mixing, corrosion, fireside deposition, combustion efficiency, and FEGT changes. The results will be utilized to confirm/expand the Phase I engineering feasibility study.

TABLE 6. SUMMARY OF REBURNING CONDITIONS TO BE EVALUATED DURING PILOT TESTS

	<u>Main Combustion (Primary) Zone</u>	<u>Reburning Zone</u>	<u>Burnout Zone</u>
Fuel	Coal (Natural Gas in Baseline)	Natural Gas, #6 Fuel Oil, Coal	N/A
Fuel Split	75 - 85%	15 - 25%	---
Stoichiometry	1.10	0.8 - 0.95	1.15 - 1.3
Residence Time	0.3 sec	0.5 - 0.7 sec	0.6 - 0.9 sec

The major areas of technical uncertainty which were identified in the feasibility case studies and will be evaluated during the pilot tests include:

- NO_x reduction potentials of the reburning fuels when operating in a cyclone boiler environment of high initial primary NO_x levels, low char carryover to main furnace, and large thermal gradients between lower and upper furnace
- Optimization of process parameters for cyclone application
- Effects on solids deposition in the upper furnace and convective section
- Corrosion throughout the furnace
- Unburned carbon, especially during coal reburn tests

CONCLUSIONS AND RECOMMENDATIONS

- Review of the cyclone boiler population shows that reburning technology to reduce NO_x emissions is applicable from the standpoint of furnace residence time availability. Only the small (<80 MW) single-wall fired units appear non-conducive to reburning.
- Criteria for main, reburning, and overfire air zone residence times and stoichiometries have been determined for cyclone firing as follows:
 - Main Zone 1.1 stoichiometry, 0.15 to 0.3 second
 - Reburning Zone ... 0.85 - 0.95 stoichiometry, 0.45 - 0.7 second
 - Overfire Air Zone . 1.16 - 1.2 stoichiometry, 0.65 - 0.9 second
- Nominal 50 - 60% NO_x reductions can be expected from existing cyclone-equipped boilers. Typical uncontrolled NO_x emissions from cyclones are 0.8 - 1.8 lb/10⁶ Btu.
- Corrosion potential within the cyclone barrel when applying this technology may be avoidable through recommended modifications to the coal/air flow control system. Additional protection may be necessary in the main furnace near the reburning ports if coal is utilized as the reburn fuel. The pilot-scale tests will assess the corrosion potential.
- Although the additional boiler impacts such as changes in FEGT, deposition, unburned carbon, steam temperatures, and boiler efficiencies are expected to be minimally impacted, pilot/full-scale testing must be performed to validate these assumptions.
- The costs to apply reburning to cyclone-equipped units for different reburning fuels are estimated as follows (total capital cost; 10-year busbar power cost): gas - \$15.2/kW, 1.6 mills/kWh; oil - \$22.3/kW, 4.0 mills/kWh; coal - \$34/kW, 1.8 mills/kWh. The corresponding gas and oil fuel costs used to determine these values are \$2 and \$3/10⁶ Btu, respectively. No gas pipeline is included. When evaluating coal as the reburn fuel, this study assumes that the coal reburn fuel is the same as the main cyclone coal.
- If no local gas pipeline is available, the capital and 10-year power costs increase to \$44.4/kW and 2.5 mills/kWh, respectively. This evaluation assumes a fuel cost of \$2/10⁶ Btu and a \$3 million cost for a 10-mile long gas pipeline.
- The reburning fuel type has a major impact on the economics of this process. Assuming that on-site gas is available (approximately 20% of total heat input), capital cost expenditures favor gas as the reburn fuel, with coal being the most costly. If an appropriate 10-mile long gas pipeline is necessary, gas becomes the most expensive capital cost choice, while oil would be the most cost-effective. The 10-year levelized costs are strongly (70 - 90%) fuel cost dependent and vary depending on the specific situation.
- Although the study assumed all three fuels were comparable with respect to reducing NO_x , pilot-scale tests must confirm this along with any associated detrimental boiler side effects. Thus, after this technical evaluation of the three reburn fuels is complete, a combined cost/technical evaluation can be performed.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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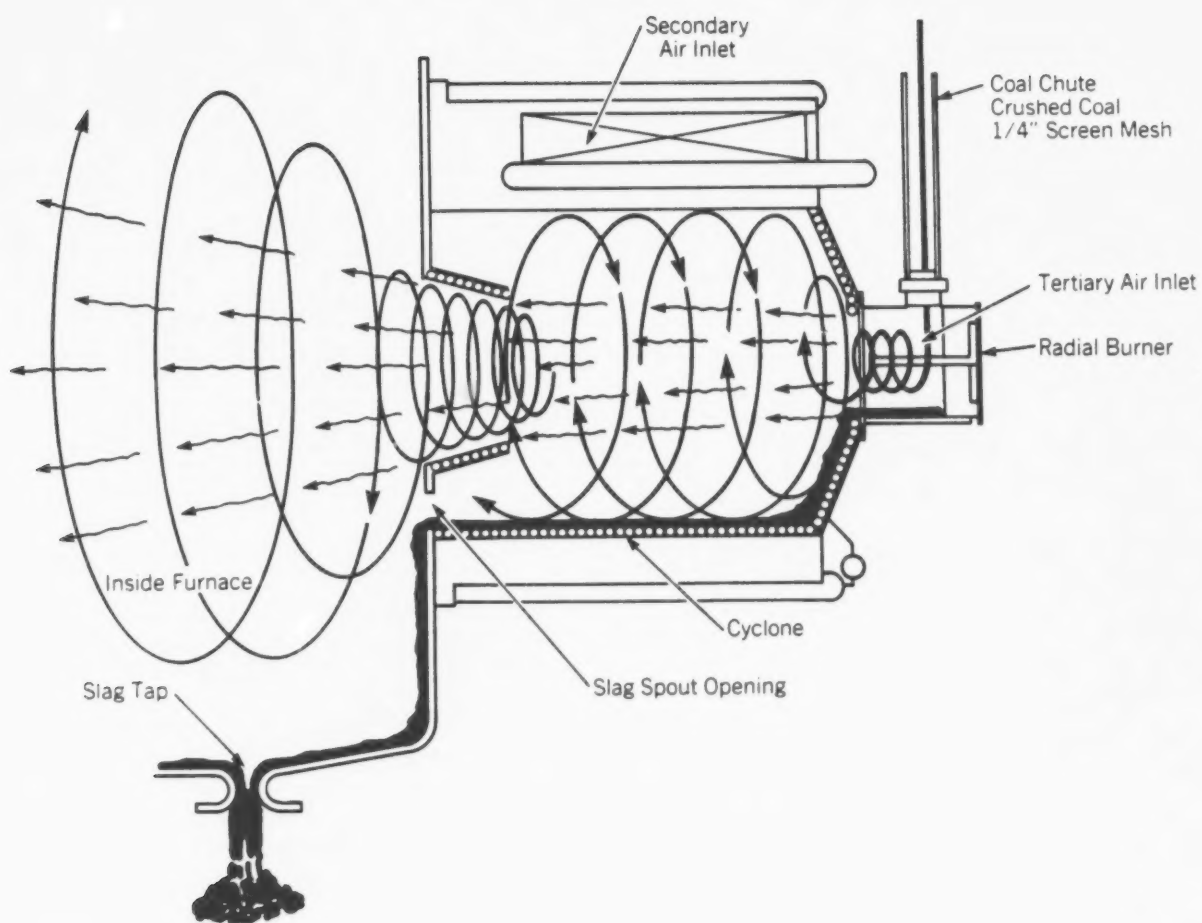


Figure 1. Cyclone Furnace

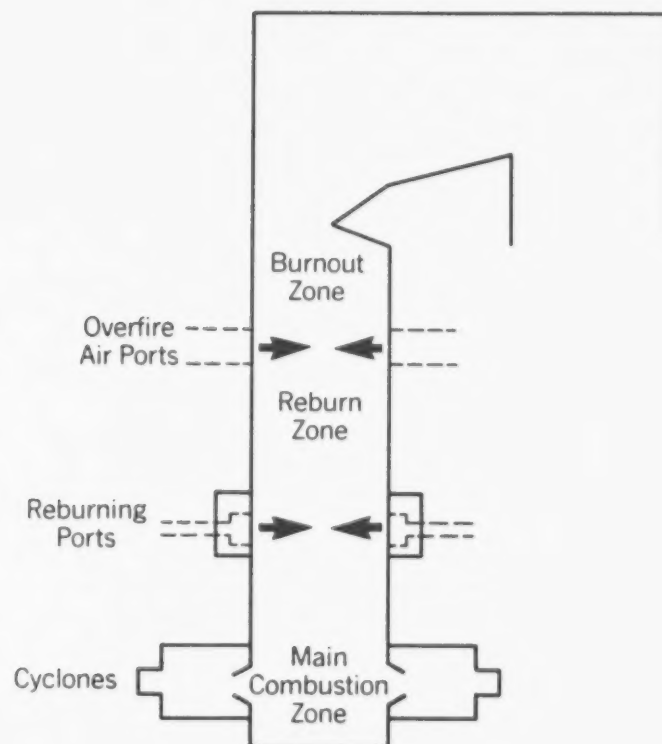


Figure 2. Reburning Process

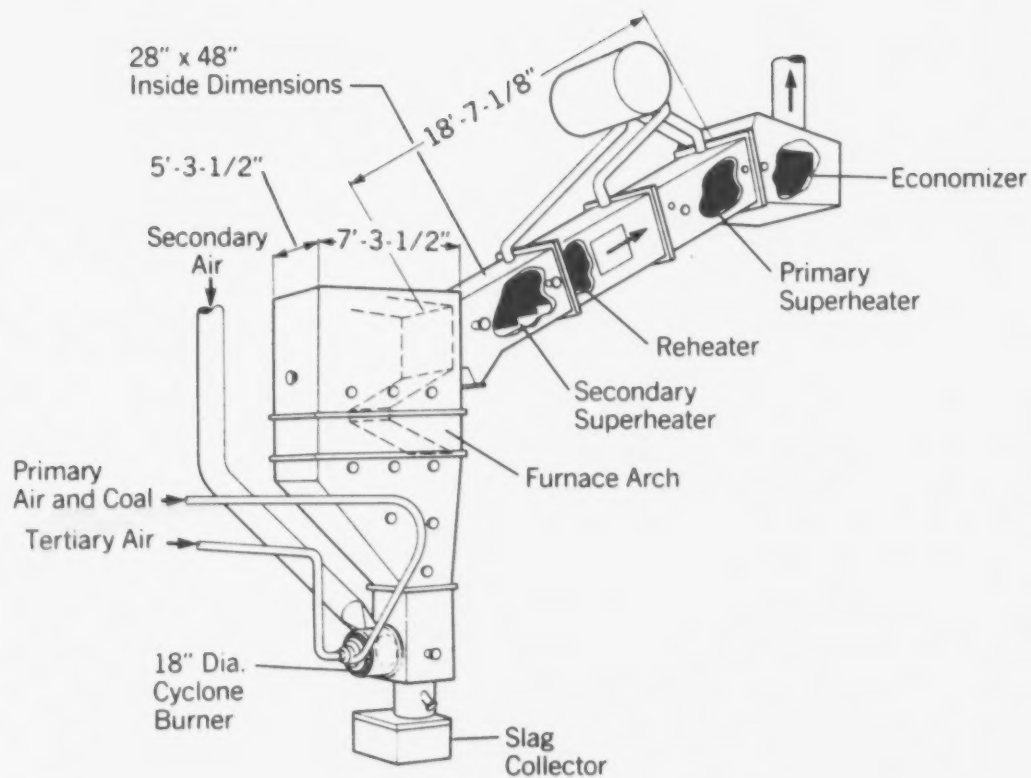


Figure 3. Babcock & Wilcox Small-Boiler Simulator (SBS)

NO_x CONTROL OPTIONS FOR COAL-FIRED CYCLONE UTILITY BOILERS

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ABSTRACT

The implementation of stringent NO_x regulations in Japan and West Germany has increased the probability of NO_x control provisions in acid rain legislation in the U.S. The economic impact of this proposed legislation is a serious concern to utilities with cyclone units because they have high NO_x emissions and very few cost-effective retrofit options. This paper highlights an EPRI study directed at evaluating NO_x control options ranging from conventional and advanced combustion modifications to low-NO_x slagging combustors, reburn technology and flue gas treatment. The first phase of the study included a review of cyclone NO_x emission characteristics, their dependence on boiler design and operating parameters, and a comparison to other unit designs. Prior attempts to reduce cyclone NO_x emissions by means of combustion modifications were evaluated and constraints to low-NO_x operation identified. These design and operating constraints included reduced combustion gas temperature, slag capture and slag viscosity control, high temperature corrosion, and carbon burnout. The relative NO_x reduction potential and operating constraints of several potential retrofit NO_x control concepts were then compared on a preliminary basis to determine which concepts exhibited the most promise. A more detailed evaluation of these concepts is continuing including brief technical and economic comparisons to alternative NO_x control options for cyclone units.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

NO_x CONTROL OPTIONS FOR COAL-FIRED CYCLONE UTILITY BOILERS

INTRODUCTION

The electric utility industry is the source of almost 30 percent of the national emissions of nitrogen oxides, with three-quarters of these emissions generated by coal-fired power plants. Approximately 85 percent of these coal-fired emissions arise from older pre-NSPS (New Source Performance Standards) units. Unfortunately, coal-fired utility boilers with a cyclone furnace design represent more than 26,000 megawatts of installed capacity and are a source of approximately 18 percent of these NO_x emissions.

In this regard, cyclone boilers represent a unique NO_x control problem that is not readily solved with conventional combustion modification techniques. The very intense combustion in the cyclone at high flame temperatures results in NO_x emissions often in excess of 1,000 ppm (1.4 lb/MMBtu). The air-rich environment in the cyclone leads to high fuel nitrogen conversion and thermal NO_x formation. The high heat release rate per unit area required to maintain slag flow within the combustor also enhances the formation of thermal NO_x. Although tangentially fired and wall-fired dry bottom units already have several retrofit NO_x control options from which to choose (e.g. low-NO_x burners, overfire air ports, burners out-of-service), no retrofit NO_x control options have been commercially demonstrated for cyclone units. Options such as reburning and selective catalytic reduction NO_x controls are being considered, but their high capital and/or operating costs are a drawback for units already 20-30 years of age.

Since combustion modifications have historically been a cost-effective means of NO_x control, EPRI sponsored a study to reassess their potential as a retrofit control measure for coal-fired cyclone units. The objectives of the study were to: 1) establish cyclone operating constraints that impact low-NO_x operating modes; and 2) evaluate the NO_x reduction potential and applicability of conventional and advanced NO_x control options to cyclone units.

COAL-FIRED CYCLONE NO_x EMISSIONS

In order to fully assess the applicability of conventional NO_x control methods, it is important to develop an appreciation for the differences in the design and NO_x emissions characteristics of pulverized coal and cyclone boilers. The combustion intensity per unit volume in a 10-foot cyclone combustor is typically 450,000 Btu/hr-ft³, whereas the typical heat release in a pulverized coal-fired unit is 20,000 Btu/hr-ft³. In addition, the heat absorption through the cyclone combustor walls is relatively low (40,000 to 80,000 Btu/hr-ft²), primarily because of the small surface area and the insulating effect of the liquid slag layer. A majority of the crushed coal is burned on the wall in a cyclone, as opposed to suspension burning in a pulverized coal-fired boiler. The high combustion intensities and long residence times at peak temperatures in a cyclone are conducive to slag flow, but also contribute to high thermal NO_x formation and fuel bound nitrogen conversion. A preliminary analysis of baseline emissions data for cyclone units suggests that the correlation of NO_x with combustion intensity may be a linear extrapolation of pulverized coal unit data to the much higher cyclone combustion intensities.

Coal-fired cyclone boiler NO_x emission data is very limited, and most of it was acquired in the early 1970's when chemiluminescent NO_x analyzers were not yet widely used. In spite of the associated data scatter, a brief assessment of baseline NO_x emissions indicates that the NO_x sensitivity to excess oxygen for some cyclone units is more than twice that of pulverized coal (PC) units. Thus, a one percent change in excess O_2 causes a 15-20 percent change in NO_x in cyclone units but only a 10 percent change in typical PC units. The sensitivity of NO_x emissions to unit load (MW or steam flow) is also greater for cyclone units, which exhibit a 10-15 percent reduction in NO_x with a 10 percent load reduction, whereas PC units experience only 5 percent reduction. This behavior is another indicator of relatively high thermal NO_x formation. Qualitative estimates indicate that as much as 50 percent of the NO_x emissions from some units may be thermal in origin (Macek, 1978). This suggests that NO_x control measures that are traditionally less effective with pulverized coal combustion, due to the predominance of fuel NO_x , may prove to be more effective on cyclone units.

POTENTIAL CYCLONE NO_x CONTROL OPTIONS

The primary parameters associated with NO_x formation and control are the local stoichiometry (excess oxygen level), peak gas temperature, and residence time. Since the gas temperature is constrained by the need to maintain slag flow and the residence time is fixed by the cyclone geometry and firing rate, the primary parameter available for thermal NO_x control is the excess oxygen concentration. However, the excess O_2 and peak gas temperature cannot be controlled independently. The application of NO_x control to a cyclone unit requires careful consideration of not only the local combustion stoichiometry, but the many operational and performance considerations associated with slag flow, corrosion, heat balance, liquid iron formation, etc. that are much more critical than on conventional PC units.

Because of these constraints, retrofit technologies have focused on removing the NO_x once it is formed (essentially reburning, but selective catalytic reduction (SCR) and ammonia or urea injection are also relevant), or by minimizing the oxygen availability as well as the peak flame temperature within the cyclone (i.e., advanced staged slagging combustors (ASSC), or conventional and advanced combustion modifications). A comparison of these technologies on the basis of NO_x reduction potential and order of magnitude costs is shown in Table 1. As none of these technologies have been demonstrated on a U.S. cyclone boiler, these figures are only estimates based on applications of the technology to coal-fired utility boilers of different configurations. From this comparison, three general levels of NO_x emissions reductions, as well as costs, can be distinguished. The first level includes combustion modifications and is anticipated to be capable of providing up to 40 percent NO_x reductions at costs on the order of \$15 to \$20/kW or less. The second level is comprised of reburning and ammonia or urea injection, which may potentially achieve reductions from 40-60 percent, at costs ranging from \$12-\$34/kW. Finally, SCR and ASSC make up the third level, which can potentially provide 50-80 percent NO_x reductions, albeit at significantly higher costs on the order of \$100/kW. It should be noted, however, that these costs, on a \$/kW basis, may be significantly higher for those units smaller than 500 MWe.

From Table 1, SCR is shown to not only be very capital intensive, but to also have high operational costs. Although selective non-catalytic reduction (SNCR) using ammonia or urea injection at around 1750 F is much less capital intensive, it is also less effective than SCR. Overall NO_x reductions are residence time and mixing dependent and may also involve trade-offs to minimize

ammonia breakthrough. For example, NO_x emissions reductions from two SNCR applications on cyclone boilers in Germany have ranged from 25-35 percent to approximately 80 percent. It should be noted, however, that the latter case is unique from the perspective that it contained a flue gas pass of long residence time, near optimum temperature, and low gas cooling rate. These characteristics are not typical for U.S. design cyclone boilers. In applications with high sulfur coals, ammonia based processes may also suffer from excessive deposits of ammonium sulfate/bisulfate on the air preheater.

Advanced staged slagging combustors, a retrofit burner technology that evolved from the former MHD programs, are currently being evaluated in demonstration programs which are addressing remaining scale-up issues as well as retrofitability to utility boiler systems. Very preliminary estimates of the capital costs for retrofitting this technology to cyclone utility boilers indicate the economics to be of the same order of magnitude as SCR (Cascone et al., 1986). These costs, however, have not been refined by the ASSC manufacturers due to the site specific nature of individual retrofits.

Reburning, the only remaining option for achieving 50 percent NO_x reductions at intermediate costs has become the subject of several cyclone demonstration projects due to the potential suitability of a majority of cyclone boilers with respect to residence time above the anticipated reburning zone. The costs associated with reburning, however, are very fuel specific and may vary depending upon whether the fuel of choice is available at the station (Maulbetsch et al., 1986).

As each of the aforementioned technologies represent relatively high capital and/or operating costs, the current program was initiated to evaluate the possibility of applying combustion modifications to a cyclone in order to achieve a moderate level of NO_x emission reductions at a relatively low cost. These approaches have historically been very cost-effective, and are thus anticipated to provide cost-effective options for cyclone boilers, as well, although at somewhat higher costs due to measures required for corrosion prevention and slag flow control.

CONVENTIONAL NO_x CONTROL OPTIONS

PRIOR FIELD TEST EXPERIENCE

Staged combustion or off-stoichiometric firing is one of the most common combustion methods for NO_x control on gas and oil-fired utility boilers, which are dominated by thermal NO_x . However, industry concerns regarding furnace corrosion, resulting from localized reducing atmospheres with high sulfur coals containing iron, prevented any significant testing of the staged combustion firing concept on cyclone units. The more recent use of low sulfur western coals, as well as a better understanding of the role of tube metal temperature in the corrosion process suggests that the concept may have new applicability in reducing NO_x emissions on cyclone boilers. A review of previous two-stage combustion tests performed during the 1971-72 time period also suggests some optimism in this regard.

Cyclone staged combustion tests were conducted at three utilities by B&W with the capacities and coal descriptions listed in Table 2. The use of a North Dakota lignite at Test Site A required supplemental oil firing to maintain temperatures, substantiating the importance of coal properties in determining the applicability of any given NO_x control technology to a cyclone burner. At Test Site B, the staged combustion testing only involved one of five cyclones, with

staged air addition occurring through an existing gas recirculation port above the staged cyclone. The gas recirculation ports above the remaining cyclones were blanked off. As this firing configuration did not produce good mixing and carbon burnout, the results were difficult to interpret with respect to NO_x reduction potential. The important factor realized from this testing, given an appropriate coal, was the ability to stage a cyclone at 85 percent theoretical air without supplementary gas or oil to sustain cyclone firing at full load. At Test Site C, optimization of the staged air addition provided a more sound basis for judging the NO_x reduction potential of staged combustion in a cyclone unit.

The boiler at Test Site C is a 60 MW radiant unit fired by two, 9-foot cyclones. For the staged combustion tests, four staged air ports were installed through the front wall at the "corners" of each cyclone (Figure 1). The air ports were angled to direct the staged combustion air flow towards the centerline of the throat discharge from the cyclone. The staged combustion tests were run on both gas and coal fuel with a first-stage stoichiometry of approximately 85 percent theoretical air. Although fired almost a year in this manner, a high sulfur bituminous coal was only burned for approximately 20 days. Very few operational problems were encountered during the staged combustion tests except for some "slag eyebrows" that developed over the NO_x ports when fired with coal. With the NO_x ports in use, the coal fire was reported to be bright with no noticeable loss of ignition. Slag tapping from the cyclones and furnace were also normal. Inspection of the cyclones at the conclusion of the test period revealed no noticeable tube metal wastage.

NO_x reductions of 50 percent were obtained with gas firing and approximately 30 percent with coal firing under staged conditions. These successes were achieved without any sacrifice in excess O_2 , which sometimes occurs with staged combustion. Although long-term feasibility issues need to be addressed before accepting this retrofit option, these tests provide very valuable data on the NO_x reduction potential of combustion modifications. Conceivably these could be achieved by different modifications, but potentially with equally attractive NO_x results.

Staged combustion is an attractive NO_x control technique because it affects both fuel and thermal NO_x . Some of the primary retrofit considerations are the installation of the staged air ducts and the change in cyclone combustion conditions due to fuel-rich operation. Other NO_x control techniques are primarily effective in controlling only the thermal NO_x emissions. Although the NO_x reduction potentials of many thermal control techniques are not as great as staged combustion, they often can be implemented with minimum advanced preparation because they do not require staged air ports. Conventional techniques commonly considered to be effective for thermal NO_x control include:

- flue gas recirculation (FGR),
- reduced air preheat, and
- water injection

Their effectiveness, which is determined by their ability to reduce overall peak flame temperature is presented in Figure 2 as a function of effective cooling (Btu/lbm fuel). To avoid the questions associated with determining the fuel nitrogen NO_x component in coal and oil flames, only gas-fired field test data were used in the evaluation. From this curve, approximations can be made of the total NO_x reductions in a coal-fired boiler given an estimate of the thermal NO_x contribution to the total emissions. The level of NO_x reduction that may

actually be achievable in a cyclone boiler, however, is constrained by operational limitations which include the ash T₂₅₀, pressure drop (fan capacity), and flame stability.

The total NO_x emission reductions in Table 3 were estimated, assuming a 50:50 split between fuel and thermal NO_x. The NO_x control potential of FGR on cyclone boilers is anticipated to depend very much upon how it is employed. For conventional flue gas recirculation into the secondary air, total NO_x reductions (fuel + thermal) of 15-20 percent are expected as a minimum with 10-15 percent flue gas recirculation. Other options for utilizing FGR for NO_x control, demonstrated at the pilot scale indicate potential NO_x reductions of 18-30 percent are also achievable with introduction of FGR into the primary air (Tidona et al., 1983). However, until these higher NO_x reduction potentials are actually demonstrated on coal-fired cyclone combustors, it is more appropriate to use a conservative estimate of a 20 percent total NO_x reduction at a 15-20 percent FGR rate for cyclone units with baseline emissions in the 1000 ppm range.

As with FGR, reduced air preheat and water injection control NO_x by reducing the peak flame temperature within the cyclone. The primary operational limitation to these approaches is in maintaining a temperature sufficient to promote slag flow within the cyclone. Combustion stability at reduced temperatures may also become a consideration in some situations, depending upon fuel type and boiler design. Generally, reduced air preheat and water injection are NO_x control options that frequently fall near the bottom of a priority list because of their adverse impact on boiler operating efficiency. Water injection significantly increases the latent heat stack losses in addition to the sensible heat loss caused by the reduced heat recovery. Total NO_x reductions of only 10-15 percent are anticipated to be achievable through either of these approaches.

ADVANCED NO_x CONTROL OPTIONS

The assessment of NO_x control options that had not been evaluated previously involved a fresh approach to NO_x control for cyclone units. Retrofit options were developed from fundamental principles rather than historical constraints. One impetus for this approach was the recognition that substantial advances have occurred in coal combustion NO_x control in the 15 years since the original cyclone combustion modification field test programs were conducted. Therefore, it was appropriate to reexamine cyclone boiler NO_x control in light of the intervening technological progress.

The identification of promising NO_x control options for cyclone units was approached by:

- analyzing the effect of variations in critical process parameters on NO_x formation
- establishing critical process constraints
- defining the acceptable range of key operating parameters
- estimating the potential NO_x reduction benefits.

It should be emphasized that this task was primarily a conceptual design screening study at a very fundamental or preliminary level to identify promising options. The options were evaluated only on a qualitative or semi-quantitative

basis, as a prelude to a more detailed preliminary design study that would follow. The primary emphasis was on identifying concepts that met the criteria listed below:

- Maximize the use of existing combustion equipment
- Minimize the number of penetrations to the main furnace tube wall or cyclone combustor
- Assign a high priority to concepts that have a prior experimental basis for the potential NO_x reductions (i.e., either laboratory scale or field test data demonstrating the reduction mechanism, preferably on coal fuel)
- Minimize unit outage time for retrofit

The initial expectation at the start of the study was that one or two promising NO_x control options would be defined for evaluation in a concluding final technical feasibility evaluation. However, six promising concepts were identified with several variations that were grouped into three major categories:

- Rich-Lean Staged Combustion
(fuel-rich first stage followed by burnout with secondary air addition)
- Lean-Rich NO_x Destruction
(fuel-lean combustion followed by NO_x destruction with fuel addition)
- Burner Flue Gas Recirculation
(application of flue gas recirculation in the combustor to reduce thermal NO_x formation)

The first step in the assessment task, after identifying several design concepts in the categories listed above, was to analyze the effect of variations in critical process parameters on NO_x formation. The primary objective was to define the process operating boundary conditions as defined by carbon utilization, slag flow, and corrosion constraints. Some examples of these issues for the three major categories are discussed in the sections that follow.

RICH-LEAN STAGED COMBUSTION

The primary issues/parameters associated with this NO_x control approach are first-stage stoichiometry control, cyclone heat rejection, coal heating value and ash properties, carbon utilization, slag flow, and corrosion control. Japanese and U.S. studies of cyclone NO_x control (Ichikawa, M. et al., 1983 and Krippene, B., 1986) have shown that minimum NO_x formation occurs at first-stage combustion stoichiometries of 0.7 or less (Figure 3), similar to a pulverized coal diffusion flame. However, operation at too low of a stoichiometry can result in a combustion gas temperature that may be less than the ash melting temperature, as shown in Figure 4 (e.g. dotted line at 2300 F). Therefore, trade-offs exist between achieving NO_x emission reductions through substoichiometric operation and maintaining slag flow within the cyclone. Depending upon the slope of the ash viscosity curve, the operating slag temperature band for uniform flow can be either very narrow or quite broad. In general, the cyclone must operate within a wall temperature band limited by ash carryover at the higher temperature and slag viscosity at the lower temperature (Figure 5).

If the first-stage stoichiometry is not carefully controlled and is allowed to approach stoichiometric, the combustion temperature will increase and the ash will tend to vaporize, resulting in unacceptable ash carryover into the furnace rather than slag rejection within the cyclone. The carryover due to evaporation, can be maintained below 10 percent, however, by cooling the wall to 3000 F (Reid, 1971). More importantly, excessive gas temperatures can lead to overheating of the cyclone tube walls and catastrophic failures under certain conditions. Because of the complex interaction between the gas temperature, slag temperature, slag viscosity/thickness, wall temperature, and wall heat loss, complex heat transfer computer codes are required to analyze the total energy balance on the combustor. These analyses were beyond the scope of the current project, but analyses conducted for MHD research programs (e.g. Koester et al., 1977) were used to define potential operating boundary conditions within a cyclone. The parameters and typical ranges defined for the rich-lean staged combustion mode are defined below:

First-stage stoichiometry	0.7 to 0.9
Cyclone heat rejection	5 to 10%
NO _x , ppm	250 to 450 ppm
Coal type	Bituminous, subbituminous
Ash	5 to 12%
T ₂₅₀	2000 to 2600 F
Coal size	90 to 99%, thru 4-mesh
Moisture	3 to 15%
Carbon in slag	0 to 10%
Combustion air temperature	500 to 700 F
Slag temperature, min/max	2150 to 2850 F

LEAN-RICH NO_x DESTRUCTION

A second category of NO_x control options that was considered is a lean-rich combustion process in which the NO_x reduction is accomplished by secondary fuel addition. Although this concept is similar in principle to reburning, it differs from the conventional reburning approach by injecting the secondary fuel into the cyclone, itself. Several potential design concepts are being examined in the second phase of the study to determine their adaptability to specific cyclone combustor/boiler design configurations.

BURNER FLUE GAS RECIRCULATION

The objective of this category of NO_x control design concepts was to inject recirculated flue gas into the cyclone combustor in a manner that would most effectively utilize the combustion products to inhibit the formation of thermal NO_x. Although the NO_x reductions with this design approach are expected to be less than with the two previous approaches, burner flue gas recirculation may be attractive for applications where the cyclone tube design and/or coal properties limit staging due to fuel-rich corrosion and/or reduced slag flow.

Limitations in applying FGR to cyclone combustors primarily include:

- gas temperature constraints,

- pressure drop considerations, and
- flame stability.

The principal constraint to the application of FGR is in maintaining the temperature within the cyclone, or at the slag tap, above the T_{250} . In addition, the increased gas flow may result in an adverse increase in pressure drop across the cyclone, significantly impacting current fan capacities. This latter consideration may also have unfavorable economic implications based on increased operating costs due to the larger pressure drop. In addition, the flame stability is dependent upon the recirculation of hot gases just outside of the burner throat. Thus, the degree of FGR which can be applied to a cyclone is constrained by the above considerations. Its use in combination with low excess air, however, may serve to counteract the magnitude of some of these constraints by minimizing the overall throughput and by partially offsetting the temperature reduction with near stoichiometric operation. Brief tests at Stadtwerke Dusseldorf AG (Asmuth, 1985) have indicated reductions on the order of 20 percent in total NO_x by operating with LEA and FGR in concert. The stack oxygen level was reduced from approximately 3 percent to 1.5 percent excess O_2 . The FGR was introduced into the cyclone with the primary air and coal stream. One should note, however, that this cyclone was of German design, in which the coal and primary air are introduced along a secant of the cyclone barrel, as opposed to the front of the cyclone.

EVALUATION ISSUES

A significant portion of the advanced NO_x control evaluation concerned the definition of alternative design concepts for achieving staged combustion in existing conventional cyclone combustors. More specifically, several different approaches for implementing secondary air addition were examined. Each design configuration was evaluated on a qualitative basis with regard to four general criteria including: 1) NO_x control performance, 2) combustion performance impacts, 3) ease of retrofit and 4) general retrofit issues. A more detailed listing of the evaluation criteria within these four areas is listed in Table 4. The evaluation of these design concepts is continuing with a more detailed study which will examine several different cyclone boiler design categories to determine the overall technical feasibility of the more promising retrofit options. Two major issues identified in this preliminary assessment for more detailed evaluation concerned potential fuel-rich corrosion and slag flow control in low- NO_x modes, as discussed in the following section.

OPERATIONAL CONSTRAINTS

CORROSION

Through the course of cyclone furnace development, corrosion problems have commonly been attributed to operation of the cyclones at low excess air levels. The localized reducing atmospheres were thought to promote the formation of iron and iron sulfide which led to accelerated tube metal loss and eventual tube failure. Since air-rich operation is a safe means of eliminating this problem, B&W has not supported or recommended any cyclone NO_x combustion modification that would result in reducing conditions within the furnace. Several of the low- NO_x combustion modifications were proposed, despite their dependence on substoichiometric operation of the cyclone or lower furnace, because recent experience and further analysis suggest that the feared material impacts can be managed.

Reasons for optimism in resolving the corrosion issue are based on successful substoichiometric operation with TRW's Slagging Combustor System (SCS), slagging gasifiers, and Kraft recovery boilers. In principle, the SCS is analogous to the cyclone furnace in that coal is combusted at high heat release rates within a water-cooled furnace in a cyclonic manner such that ash particles are melted and thrown out to the wall. Although the SCS uses pulverized coal and suspension burning, whereas the conventional cyclone burns crushed coal along the wall, the corrosion mechanism and means for controlling it are the same. The mild steel surface of the SCS is protected from corrosive attack by controlling wall temperatures through forced water-cooling to within a range of 300-600 F to avoid acid condensation at lower temperatures and sulfidation attack at higher temperatures. Thus, corrosion within cyclone furnaces may potentially be maintained within acceptable limits by exerting greater control over the tube metal temperatures. Normal tube surface temperatures in cyclones are currently in the range of 500-800 F, depending mainly on the steam pressure (Sage, 1986).

Kraft recovery furnaces also currently operate under conditions similar to those which would be encountered in a cyclone operating under staged conditions. Black liquor introduced into the furnace is dehydrated to form a char bed in the furnace bottom. Partial combustion of the char in a reducing atmosphere at the surface of the porous bed in the furnace releases carbon monoxide and incandescent carbon which act as reducing agents to convert the sulfate in the smelt to sulfide. In order to protect against the corrosive potential of the smelt in a reducing atmosphere of the hearth, a chrome refractory is used to prevent the molten smelt from contacting the tube metal. The cooled refractory is retained by pin studs on the water-cooled tubes.

Investigations by the Finnish Recovery Furnace Corrosion Research Committee determined that a direct correlation exists between the rate of metal loss and the tube metal temperature (Moberg, 1974). Metal loss was found to occur at a low rate with metal temperatures below 600 F. Above this temperature, corrosion occurs much more rapidly, as shown in Figure 6. Thus, in a recovery furnace as well as a cyclone, the tube metal temperature becomes the determining factor at which the iron sulfide reduction reaction occurs. With the expected temperature gradient across the tube wall, the critical metal temperature, above which corrosion potential increases rapidly, corresponds to a unit operating pressure of around 1000 psig (Dickinson et al., 1981).

Thus, maintaining air-rich conditions is not always sufficient to prevent corrosion. Control and/or modification of peak tube temperatures, however, can potentially reduce corrosion rates to within acceptable limits. Experiences with a cyclone-fired unit at the Walsum plant in Germany in the early 1960's demonstrated severe corrosion and erosion after 5000 hours operation when operated with a chrome ore/mild steel stud lining and 0.8 percent O_2 in the flue gas. Secant firing was subsequently installed in conjunction with increasing the O_2 content in the flue gas to approximately 2 percent. Although erosion problems were eliminated, corrosion of the studs and tubes became excessive after an additional 20,000 hours of operation. At this stage, the cyclones were restudded with Sicromal studs at a closer pitch and a silicon carbide refractory. This combination provided a closer match between the thermal conductivities of the stud and refractory material, thereby minimizing peak tube temperatures. Subsequent operation of the cyclone was reported to be trouble-free for over 20,000 hours without any signs of corrosion or erosion in the cyclone (Roberts, 1964).

SLAG VISCOSITY CONTROL

As noted previously, reduced operating temperatures will be associated with substoichiometric operation. Thus, slag tapping problems may become a limiting factor in establishing allowable operating stoichiometries rather than corrosion. Current utility practice for slag tapping problems encountered during air-rich operation involves reducing the secondary air flow rates. In this manner, the cyclone is operated closer to stoichiometric conditions, which serves to increase the gas temperature, and potentially reduce the slag viscosity to the point where it may be tapped. In the case of fuel-rich operation, this process is merely reversed, with secondary air flows increased toward stoichiometric operation.

An alternative means for reducing the slag viscosity uses fluxing agents to modify the viscosity-temperature characteristics of the slag. Success with modification of the ash fusion temperature by fluxing agents has been found to be dependent upon the relative levels of acidic and basic constituents in the ash. For bituminous-type ash and lignitic-type ash with an acidic content in excess of 60 percent, the viscosity of a slag decreases as the base-to-acid ratio approaches the value of one. Changes in the baseline ash fusion temperature can thus be made in either direction by shifting the base-to-acid ratio through the addition of fluxing agents such as limestone (CaCO_3) or sand (SiO_2). One should note, however, that the minimum ash fusion temperature is generally found where the acidic and basic constituents are in equal proportion. Further increases in either constituent at this point only serves to increase the ash fusion temperature, as noted in Figure 7.

Since most American coals east of the Mississippi River have ash with an acidic content greater than 50 percent, a suitable flux will be a material rich in CaO , MgO , or Fe_2O_3 . Fluxing materials with high percentages of Fe_2O_3 , however, should typically be avoided except where the iron content and sulfur content of the coal ash is very low. Some acceptable materials which have been economically used for the purpose of fluxing include limestone, oyster shells and dolomite. Other possible sources of flux material include a suitable cyclone slag or stoker refuse.

For coals having ash in which the acidic content is less than 50 percent, a suitable flux will be a material rich in silica or alumina. As these coals are generally of low quality or low rank, it is typically recommended that blending with a low fusion coal be performed instead of fluxing. When the fluxing agent takes the form of a secondary fuel with a comparable heating value, the temperature of the furnace can be maintained at a comparable level, since the heating value is not being diluted through the addition of essentially inert material. The heat loss associated with fluxing has been determined to be equivalent to approximately 1000 Btu/lb of slag going to the slag tank. Thus, even for higher acidic content coals, general practice is not to allow the flux quantity plus the solid fuel ash quantity to exceed 25 percent by weight. It should also be noted that the most effective use of fluxing agents requires that they be added on a consistent basis, preferably with the coal or in the form of a coal blend.

Most experience with fluxing has been with Eastern coals having a high acidic content, where calcium-based fluxing compounds were used. This experience dates back over the last 30 years. As of 1983, however, Willow Island Power Station (Allegheny Power System) and Gannon Station (Tampa Electric Co.) were the only cyclone stations currently using any fuel additives on a full-time basis, although several other utilities have experimented with their use on a temporary basis with mixed results. Willow Island's current practice is to add between

2-6 percent limestone as the coal is brought in from coal handling. The addition of limestone has been found to adjust the ash fusion temperatures adequately, although adverse effects have been noted on the amount of ash collected by the precipitator.

The quantity of flux generally required is dependent upon the desired reduction of slag viscosity under furnace conditions, the total effective ingredients in the fluxing material, and the relative amounts of acidic constituents which it contains. Typical flux feed rates for a bituminous coal will be on the order of five percent of the coal feed rate, but are coal type and additive dependent.

An alternative approach to the use of fluxing agents, albeit similar in principle, is to blend a low and a high fusion coal such that an acceptable intermediate ash fusion temperature is obtained. The use of fluxing agents and coal blending for modifying slag viscosity-temperature relationships is a viable technology, although its success is reportedly contingent on continuous feeding at rates commensurate with the given ash analysis. Thus, fluxing agents or coal blending may be used to provide additional latitude in the operating temperature restrictions required to maintain slag flow.

FUTURE WORK

The preceding discussion has focused on two of the most important operational issues common to several combustion modifications for NO_x control in cyclone-equipped boilers. The assessment study is continuing with a more detailed evaluation of the most promising options, and the ongoing study will focus on issues concerning: 1) retrofit design and implementation, and 2) operational impact and boiler performance. More specifically, several characteristic cyclone boiler design configurations will be evaluated to determine which option offers the most cost-effective means of achieving the required fuel and/or air addition for NO_x control. This evaluation will include a detailed examination of specific boiler/burner type retrofit constraints utilizing boiler design data and drawings from characteristic units in a given boiler design category. Generic (order of magnitude) cost estimates and trade-offs will be made between the most promising options.

The ongoing study will also evaluate several of the most promising options with regard to their impact on unit operations, maintenance, boiler performance, and efficiency. Preliminary results from the corrosion and slag viscosity control evaluation were discussed previously. Subsequent evaluation activities will also consider:

- the impact on combustor performance and heat balance,
- options for improving carbon burnout,
- potential adaptability to western coals, and
- the impact on boiler efficiency.

Technical input and comments from the utility industry and the boiler manufacturer will be solicited as these evaluations are being conducted.

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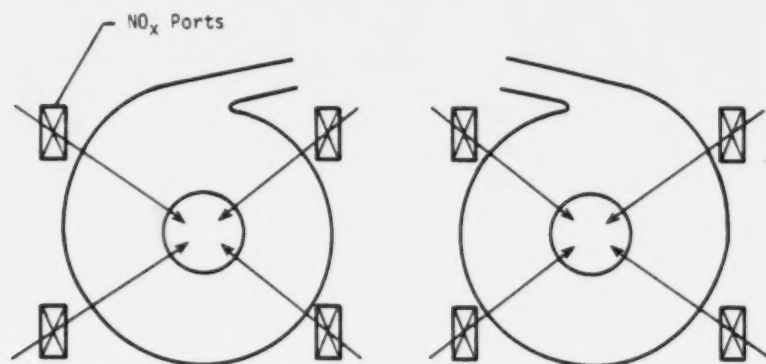


Figure 1. Sketch of NO_x Ports and Air Flow Direction at Test Site C

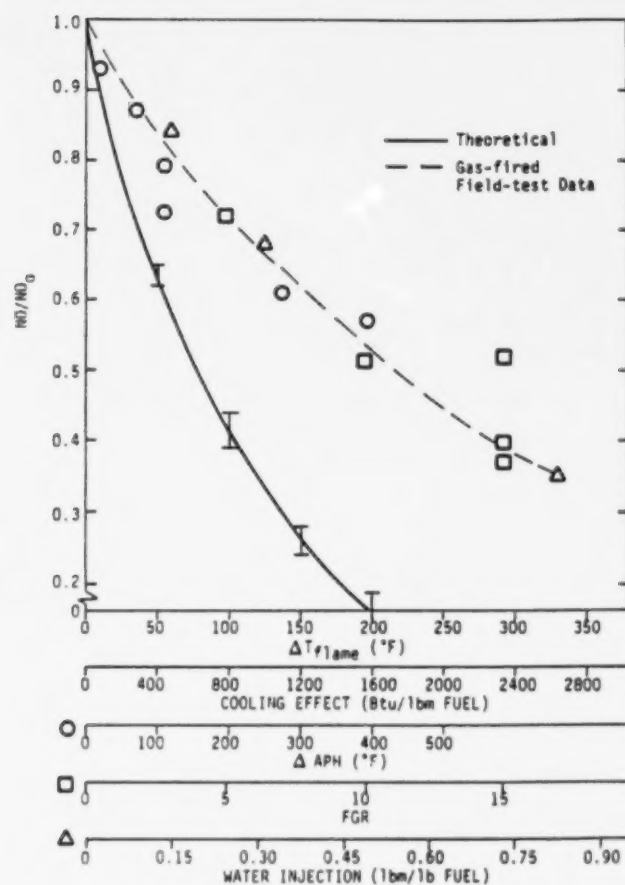


Figure 2. Comparison of Thermal NO_x Control Techniques as a Function of Effective Cooling (flow rates based on natural gas-fired conditions at 110% excess air)

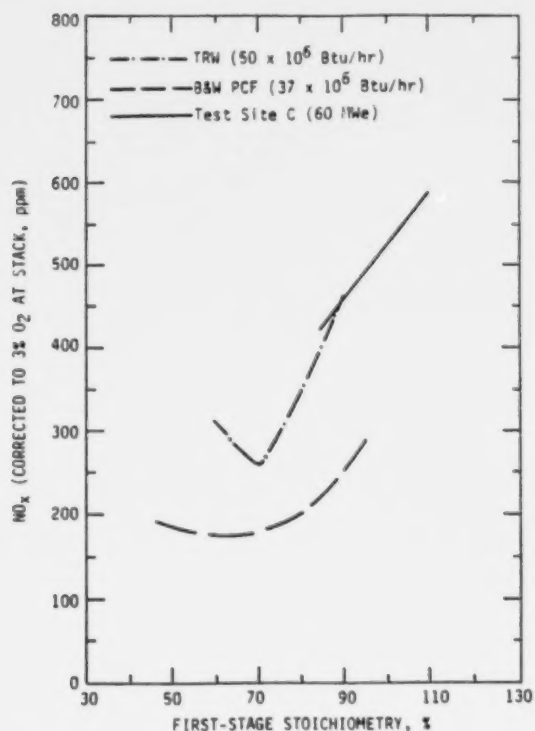


Figure 3. NO Concentration vs. First-Stage Stoichiometry

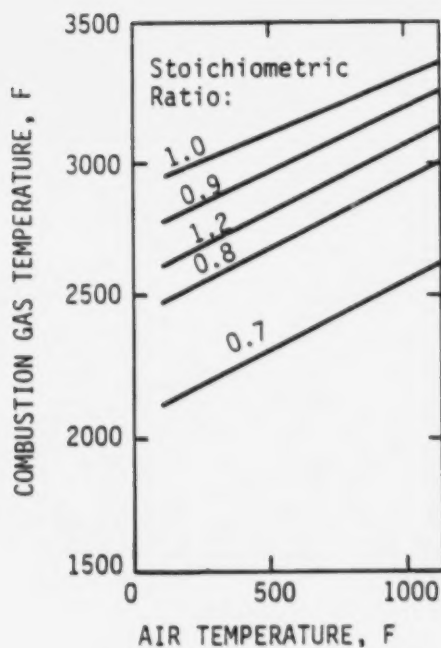


Figure 4. Combustion Gas Temperature as a Function of Stoichiometric Ratio and Air Preheat Temperature (computed) (Ichikawa, 1983)

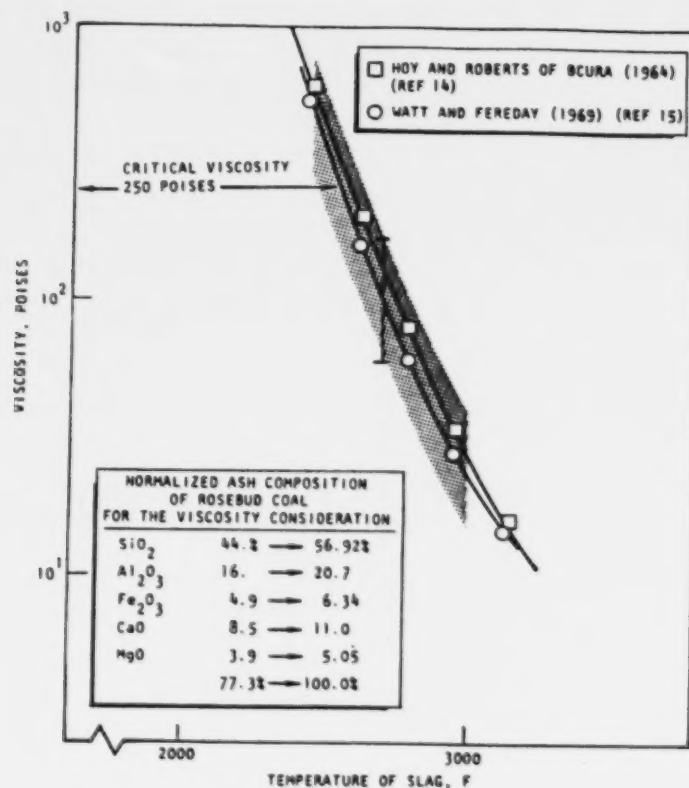


Figure 5. Slag Viscosity as a Function of Temperature for Rosebud Coal

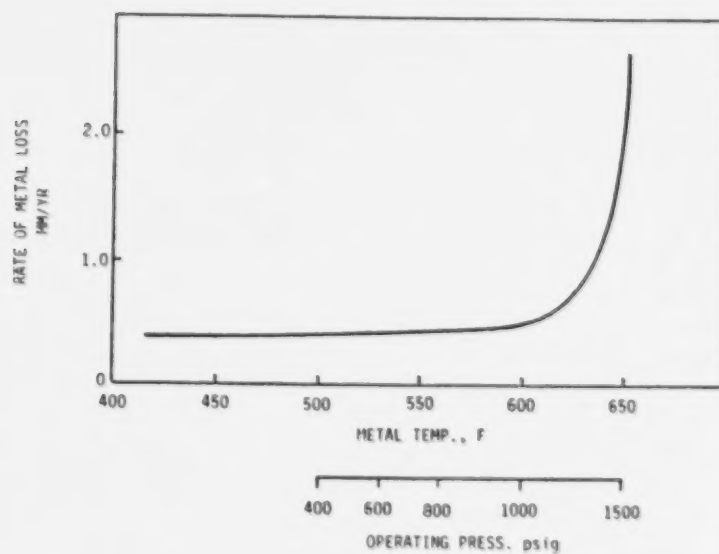


Figure 6. Corrosion Rate vs. Metal Temperature (Dickinson et al., 1981)

SLAG VISCOSITY VS. BASIC CONTENT

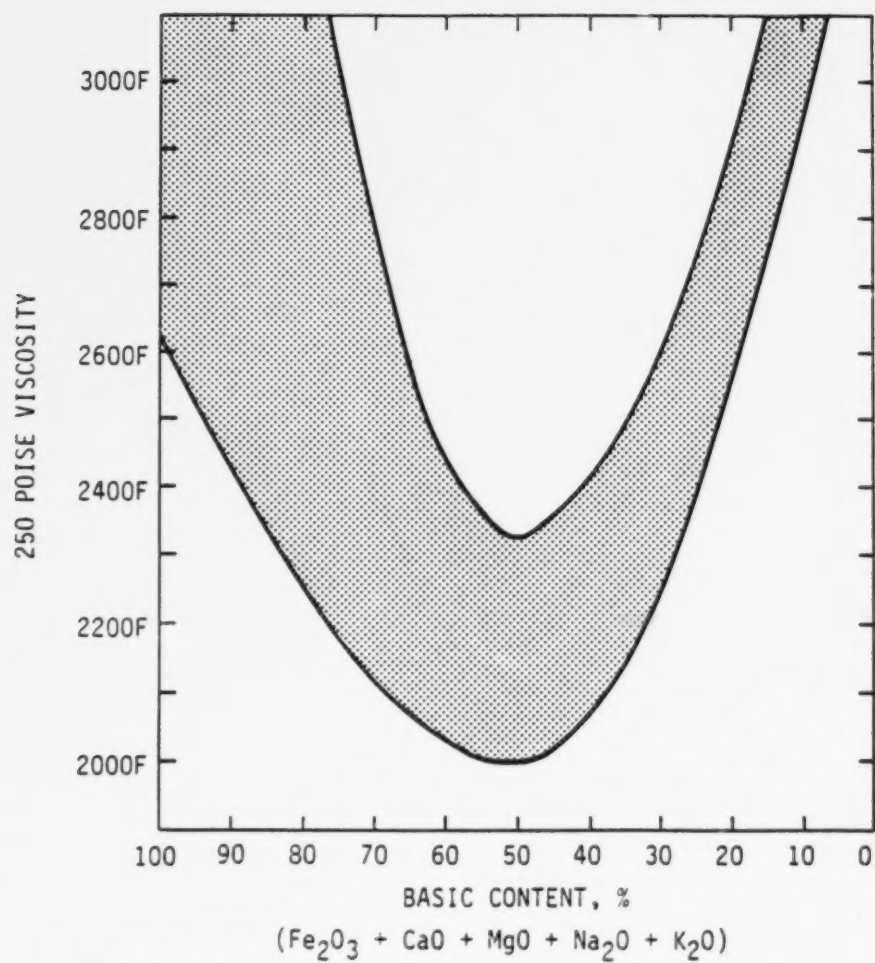


Figure 7. Range of Slag Viscosity as Measured by T_{250} and Basic Content of Coal Ash

TABLE 1. COMPARISON OF POTENTIAL CYCLONE NO_x REDUCTION TECHNOLOGIES AND ECONOMIC COSTS (JAN. 1986 \$)⁽¹⁾
(Estimates on technology under development)

Comb. Modifications ⁽²⁾	NO _x Reduction Potential Typical (z)	Maximum (%)	Total Capital Requirement (\$/kW)	10-Year Levelized Busbar Cost (mills/kWh)	References
- Cyclone	20-40	50	N.A. ⁽³⁾	N.A. ⁽³⁾	(Miller, 1985)
- PC	10-50	70	0.5-15	<1	
Reburn	40-50	60	15-34	2.0-10.0	(Maulbetsch et al., 1986)
Ammonia/Urea Inject. ⁽⁴⁾	40-50	65	12-19 ⁽⁵⁾	1.6-1.9 ⁽⁵⁾	(Miller, 1985)
Low-NO _x Slagging Combustors	50-60	70	100	N.A. ⁽³⁾	(Cascone et al., 1986)
SCR	60-80	90	60-110 ⁽⁵⁾	8-14 ⁽⁵⁾	(Miller, 1985)

(1) None of these technologies have been demonstrated in the United States, and as such, are not considered to be commercially available. The values presented are only intended as order of magnitude indications, with actual retrofit costs varying with unit size and site specific factors.

(2) No combustion modification NO_x reductions estimated or costed by other studies to date.

(3) N.A. = Not available.

(4) Urea injection costs may be significantly lower. Applicability of SNCR technology in general to high sulfur coal-fired units is in question due to ammonium sulfate/bisulfate production as well as ammonia breakthrough.

(5) Costs adjusted to reflect January 1986 dollars.

TABLE 2. COAL-FIRED BOILER NO_x CONTROL TEST SITES

Utility	Capacity	Coal	First-Stage Stoichiometry	% NO _x Reduction
Test Site A	250 MW	Lignite-0.8% S	--	--
Test Site B	175 MW	Bituminous	85	19-37*
Test Site C	60 MW	Bituminous-4% S	85	30

*Only one of five cyclones staged; emissions measurements made from side wall.

TABLE 3. POTENTIAL EFFECTIVENESS OF CONVENTIONAL NO_x CONTROL OPTIONS
(Estimates on technology under development)

NO _x Control Option	Potential NO _x Reduction (%)	Level	Considerations
FGR - Windbox	15-20	10% FGR	. Flame stability, temperature, air pressure drop
Water Injection	10-15	0.20 lb/ lb fuel	. Flame stability, temperature, & boiler efficiency impacts
Air Preheat	10	Δ150 F	. Flame stability, temperature, & boiler efficiency impacts

TABLE 4. CYCLONE NO_x CONTROL QUALITATIVE EVALUATION CRITERIA

NO_x Control Performance

- NO_x Reduction Potential
- Sensitivity to Stoichiometry Control
- Sensitivity to Coal Type
- Experimental Basis for NO_x Reduction Estimates

Combustion Performance Impacts

- Carbon Burnout
- Combustor Gas Temperature/Slag Flow
- Modified Flow Field/Combustor Aerodynamics
- Added Heat Release in Combustor
- Potential Increased Combustor Pressure Drop
- Possible Fuel-Rich Corrosion
- Effectiveness in Mixing or Staging Combustion
- Overall Boiler Efficiency

Ease of Retrofit Issues

- Additional Fans and/or Ductwork
- Additional Ports in Furnace Wall
- Interference with Structural Members
- Minimum Outage Time; Off-site Modular Construction
- Accessibility to Burner Deck
- Relative Expense of Retrofit
- Additional Dampening, Flow Control or Instrumentation

General Retrofit Issues

- Requires Dual Fuel Operating Capability
- Requires Gas Fuel on Station
- Applicable to a Wide Range of Unit Sizes and Design Types
- Convenient to Test on Interim Basis

TRW Coal Combustor -
NOx Emissions

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SUMMARY AND CONCLUSIONS

TRW, has developed an atmospheric, entrained coal combustor with significant support from DOE/PETC which can either be retrofitted to existing units or integrated with new steam generating equipment.

The concept consists of a water-cooled main combustor in which pulverized coal is burned in suspension at heat release rates approaching 1 mm Btu/hr-Ft³ of combustor volume. Combustion occurs at sub-stoichiometric conditions in order to control NO_x formation. More than 90% of the ash is removed from the combustor as a molten slag. The flue gas exiting the combustor is at a temperature near 3000°F, contains almost no carbon, only 10% of the ash, and CO & H₂ (amounting to about 15% of the original heat input). These gaseous combustibles must be burned in the host boiler and the final air, termed secondary air, is injected into the furnace through a conventional windbox/burner arrangement.

TRW has conducted a large number of tests at its Capistrano test facilities to minimize NO_x formation. The earlier determinations were made on a 10 mm Btu/hr combustor, firing Utah, Wyoming and Montana coals. The secondary air was admitted through fixed pipes and final combustion occurred in an uninsulated water-cooled chamber.

Later tests were performed in a 50 mm Btu/hr combustor, also at Capistrano. These results supported most of the earlier conclusions and provided additional insight regarding the beneficial effects on NO_x formation of controlled mixing and burning in the secondary combustion stage.

The results from both the 10 mm Btu/hr and 50 mm Btu/hr combustors indicate the following:

- NO_x emissions are chiefly a result of fuel nitrogen
- NO_x emissions are most strongly influenced by combustor main-stage stoichiometry
- NO_x emissions reach a minimum at a main-stage stoichiometry near 0.7

- At the minimum point (0.7 ϕ), other system parameters have little effect on NO_x emissions
- Emission levels increase with increasing fuel nitrogen levels
- Secondary combustion parameters affect total emission levels. Staging the secondary air by use of overfire air shows promise of additional reductions

ENTRAINED COMBUSTION SYSTEM

The complete entrained combustion system is shown in Figure 1. It consists of a small coal hopper with integral dense phase feed components, a compact slagging stage, a precombustor for boosting inlet air temperature, a slag recovery device, a short connecting duct and a secondary burner with associated controls. The system is integrated with conventional coal and ash handling systems and attached or retrofitted to new or existing heat utilization equipment.

The dense phase feed system includes a coal hopper which receives standard pulverized coal (70 per cent through 200 mesh) from a conventional mill. A flow measurement and fluidizing system maintains a controlled, dense phase fuel feed at a 10 to 1 weight ratio of coal-to-fluidizing gas.

The main slagging stage, shown in Figure 2 as part of a commercial combustor, consists of an insulated water-cooled cylinder which receives preheated air from the coal-fired precombustor and pulverized coal from the dense phase feed system. The unit is constructed of mild steel tubing in a fashion similar to typical boiler waterwall construction. Internally, the slagging stage is provided with a slag control baffle and welded studs to ensure uniform slag deposition.

A photograph of the internal slag layer adhering to the combustor walls following operation is shown in Figure 3. Note the injector located on axis and the tangential air inlet in the upper left of the picture. The slag layer covers the combustor wall to a depth of 1/2" to 3/4" and has the appearance of a black glassy material. It acts as an efficient thermal and hot gas barrier.

The precombustor is attached to the tangential air inlet of the slagging stage. It is fired with coal and is used to boost the air inlet temperature to the values desired for optimum combustor performance. Coal is fed to the precombustor from the same dense phase feed system used to supply the slagging stage.

A short duct, visible in Figure 2, connects the exit of the combustor to the secondary burner at the boiler front. This burner allows combustion air to be mixed with hot combustor gases exiting the duct. Combustion of the unburned gases is completed in the furnace volume of the heat utilization equipment. Carbon conversion is 99.5 per cent within the combustor.

BACKGROUND

The R&D of the TRW Combustor was initiated in 1975 and consisted of numerous bench-scale tests and air flow modeling to establish fluidization and flow injection parameters; a 17" I.D., feasibility unit was then fabricated and basic combustion principles were demonstrated.

In 1978 TRW constructed the Fossil Energy Test Site (FETS) at Capistrano, as shown in Figure 4. Two test chambers were built initially and a third was added in 1983.

The original facility accommodated a pressurized combustor for MHD development activities and a 17" I.D. (10 mm Btu/hr) commercial test unit; the latter is shown in Figures 5 and 6. As in the feasibility unit, this combustor was assembled from flanged sections, providing flexibility in combustor length and specific geometry. Each section was independently water-cooled, allowing axial calorimetry data to be taken during testing. A precombustor, shown in Figure 5 near the test technician, was used to boost the temperature of the incoming air stream. The combustor was elevated at 30 degrees to the horizontal, thus adding a gravity vector to aid slag flow. An air preheater, fans, ducts, a large secondary combustion chamber and facility water scrubber were added, as shown in Figure 6. Hot combustion gas, laden with very fine particulates, entered the secondary combustion chamber via a connecting duct after exiting the combustor at right angles to its axis. Secondary air was added to complete combustion of the CO and H₂-rich gas within the secondary combustion chamber.

It was on this unit that all of the early testing was conducted on NO_x emissions.

In 1983, a 34" I.D., commercial test combustor (workhorse) was designed and installed in a new test position at FETS. This combustor is normally operated at power levels of 17 to 50 mm Btu/hr (3 to 1 turndown). The workhorse combustor is shown in Figure 7 mounted on a structural frame with a 15 degree incline. The cylindrical, or slagging section of the combustor, is approximately 3 ft. in diameter and 5 ft. in length. A precombustor was attached to the rectangular air inlet noted at the top of the figure. In the workhorse unit, a combination vertical/horizontal (elbow) exhaust was used. An overview of the installation is shown in Figure 8.

The 34" combustor was further modified in late 1985 with the addition of a large boiler simulator, as shown in Figure 9. The simulator features a secondary air register, versatile furnace section and convective tube arrangement where materials, temperatures and tube spacings (gas flow velocities) can be varied. In this way, the effects of hot combustor exhaust gases containing fine particulates on typical boiler internal surfaces were ascertained. NO_x levels, following controlled secondary combustion, were studied and a sorbent injection apparatus was used to conduct experiments on SO_x reduction; these tests are continuing.

TEST RESULTS

The NO_x test results involved (in chronological order) the 10 mm Btu/hr commercial test unit, the 50 mm Btu/hr commercial test unit without the boiler simulator, and this same combustor fitted to the boiler simulator.

PHASE I (10 MM BTU/HR COMMERCIAL TEST UNIT)

The test assembly consisted of the components shown in Figure 10. The combustor operated in two stages; substoichiometric in the main stage to control NO_x and about 3% excess O₂ in the secondary combustion chamber, following the injection of secondary air. The secondary air was added only at the hot gas

exhaust location; i.e.: no NO_x ports nor distributed air addition were used in these tests. The secondary combustion chamber was a large water-cooled cylinder, 5 feet in diameter and 15 feet in length. Instrumentation ports for secondary flame characterization lined the chamber side walls and exit plate. Finally, the flue gases exiting the chamber were quenched and entered a facility type cyclone scrubber prior to the stack.

Three coals were tested during this phase of the program; Utah Emery Mine, Wyoming Powder River Basin, and Montana Rosebud. Pertinent analysis of these coals is shown in Table 1.

The most significant findings of these tests were that NO_x emissions are most strongly dependent on main stage combustor stoichiometry* and reached a minimum at $0.70 \phi_1$, indicating that NO_x formation was not a result of thermal NO_x alone. Other parameters were found to influence NO_x emissions (as will be discussed later) but none as strongly as main stage combustor stoichiometry. This trend was established by varying combustor stoichiometry and holding the following parameters constant:

- o Overall stoichiometry
- o Load
- o Preheat temperature leaving precombustor

It should be noted that stoichiometries were calculated using excess O_2 levels measured in the secondary combustion chamber and system air flow and coal flow measurements.

Figure 11 shows the results of the tests on Utah Emery coal establishing the minimum NO_x point and dependence on main stage combustor stoichiometry. Where only stoichiometry and preheat varied, the NO_x was measured at both the exit of the first stage and at the location in the secondary combustion chamber shown in Figure 10. By comparing these NO_x levels at the same dilution, the level of NO_x emissions formed in the secondary burner was determined by difference, Figure 12 illustrates these three NO_x emissions levels as a function of main stage combustor ϕ . NO_x formed in the secondary burner decreased as combustor stoichiometry increased. On the other hand, NO_x formed in the combustor increased as combustor stoichiometry increased. The sum of these gave total NO_x with a minimum at $0.70 \phi_1$. If the NO_x measured at the end of the secondary combustion chamber had continued to decrease below a combustor stoichiometry of 0.70, the NO_x could have been attributed to thermal NO_x formation. The increase in emissions below 0.70 indicated that fuel nitrogen conversion to NO_x precursors was taking place.

The secondary burner NO_x emissions resulted from NO_x precursors produced in the combustor (nitrogen compounds such as ammonia and hydrogen cyanide) which were oxidized to NO_x in the secondary burner.

*Stoichiometry here is defined as:

$$\text{Stoichiometry, } \phi = \frac{\text{Available Oxygen}}{\text{Oxygen required for stoichiometric combustion}}$$

Equilibrium calculations supported the conclusion that ammonia and hydrogen cyanide in the combustor correspond to the NO_x formed in the secondary burner.

OVERALL STOICHIOMETRY

Figure 13 shows the factor by which NO_x is increased as both main stage stoichiometry and overall stoichiometry are varied.

The fact the NO_x emissions plotted to a straight line at a main stage stoichiometry near 0.70 indicated that NO_x at the minimum point is independent of parameters other than main stage combustor stoichiometry. However, at higher main stage stoichiometry, NO_x depended on several other parameters, as well.

COMBUSTOR LOADING

Figure 14 shows the effect of variations in combustor throughput on NO_x formation, at various main stage stoichiometric levels. The " NO_x Factor" is a multiplier referenced to the NO_x level measured at a main stage ϕ of 0.70. Combustor loading had little effect at ϕ near 0.7. The test points at higher stoichiometries had too much scatter to establish clear trends within the narrow parametric range studied. The effect of loading is discussed further in the 50 mm Btu/hr combustor tests.

COMBUSTOR PREHEAT TEMPERATURE

The last variable tested was the air temperature exiting the precombustor and entering the main stage. The results are shown in Figure 15. The negatively sloped lines give strong evidence that the NO_x formed is from fuel- and not thermal-nitrogen.

PHASE II (50 MM BTU/HR COMMERCIAL TEST UNIT WITHOUT BOILER SIMULATOR)

The testing of the 50 mm Btu/hr (34" I.D.) combustor was initiated in early 1984 with DOE/PETC funding and the equipment arrangement was as shown in Figure 16. The final burning stage occurred in the "afterburner", which consisted of a water-cooled, unlined cylinder, 36 inches I.D. and 15 feet long. Secondary air was admitted radially via pipes and the products of combustion were quenched prior to the scrubber. NO_x samples were taken just before the quench chamber.

An analysis of the coals tested in this larger combustor is shown in Table II. A summary of the test results for the 50 mm Btu/hr unit compared to the 10 mm Btu/hr unit is shown in Table III.

A comparison of NO_x emission data between the 50 mm Btu/hr and the 10 mm Btu/hr combustors using Wyoming coal is shown in Figure 17. The steeper slopes associated with the larger combustor is indicative of the improved ignition and burning characteristics compared to those observed in the smaller combustor. In general, head-end temperatures were higher with all coals tested.

As would be expected, NO_x levels increased with fuel nitrogen, as shown in Figure 18. The " NO_x Factor" is a multiplier referenced to the NO_x value measured with Wyoming coal. The trend was observed in the smaller combustor as well, but was not so clearly defined due to the wider variations in head-end combustor characteristics in the smaller unit.

The effect of combustor stoichiometry for high fuel nitrogen Pittsburgh No. 8 coal is shown in Figure 19. Once again, the NO_x minimum occurred at a ϕ of 0.7.

PHASE III (50 MM BTU/HR COMMERCIAL TEST UNIT WITHOUT BOILER SIMULATOR)

In late 1985 the afterburner on the 50 MM Btu/Hr combustor, shown in Figure 16, was replaced with the boiler simulator indicated in Figure 20. The simulator is water-cooled and contains refractory-lined sections that can be modified to alter heat transfer rates along its length. A convective section in the aft end contains a removable tube bundle array in which materials, temperatures, tube spacings and gas velocities can be varied.

A commercial secondary burner was also installed, in which the final air for combustion was admitted around the combustor discharge products. Air could now be admitted in a more uniform and controlled manner than was possible with the afterburner. Moreover, the heat transfer rate to the walls more closely duplicated commercial industrial - type boilers. Testing, funded by DOE/PETC, was initiated in early 1986.

The result was a significant decrease in NO_x production when firing the same coals as were tested in Phase II. As shown in Figures 21 and 22 (Pittsburgh No. 8 and upper Freeport coals, respectively), the Phase III NO_x levels was as much as 30% less at the Full rating of 50 mm Btu/hr. The figures also show the further reductions resulting from reduced combustor loadings.

FUTURE PROGRAM

The NO_x testing to date was achieved with 100% of the remaining air admitted through the secondary burner. Future tests planned in 1987 and beyond will explore the effects on NO_x production of air staging within the boiler simulator.

TRW has also retrofitted a 30,000 lb/hr (steam) industrial boiler in Cleveland, Ohio with a single 40 mm Btu/hr combustor. The unit is about to complete its first 4000 hours of operation. The next phase of the program, which will demonstrate long-term emissions control techniques, will commence in April, 1987 and will be funded in part by the Ohio Coal Development Office. The NO_x control will consist of a fully adjustable secondary burner, coupled with two overfire air ports located in the front wall, just above the secondary burner. Initial results should be available after mid-year.

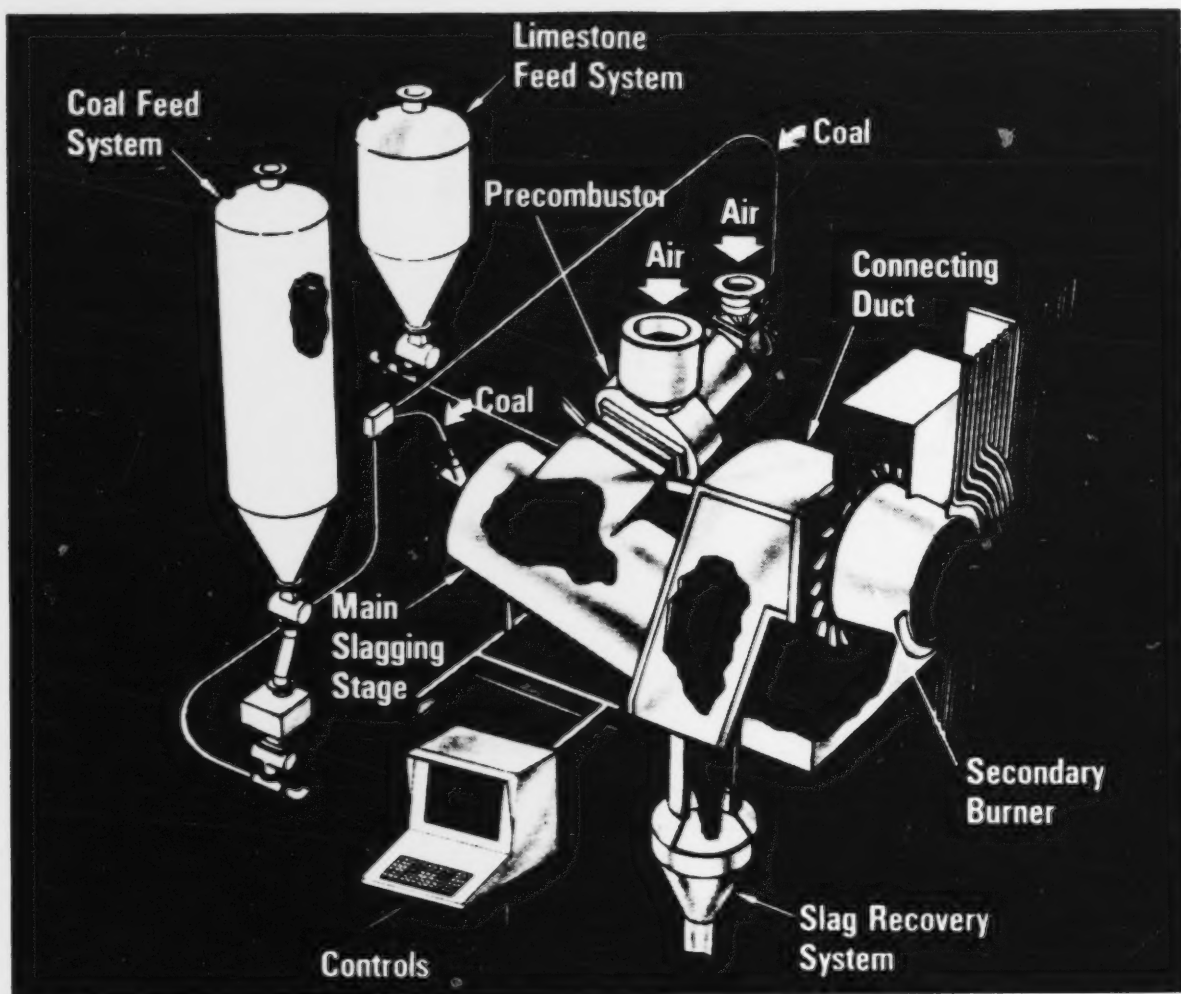


Figure 1. TRW Coal Combustion System

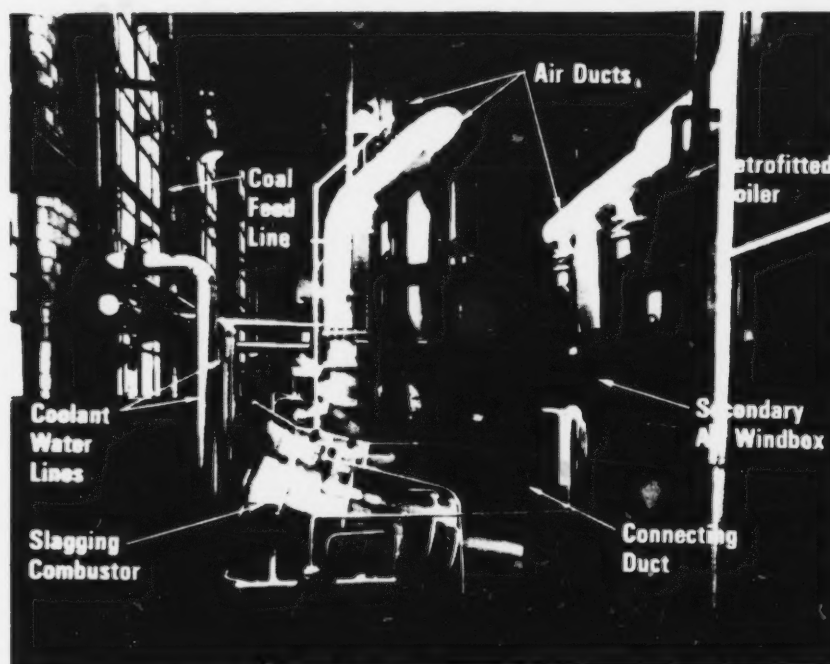


Figure 2. Installed Coal Combustion System



Figure 3. Equilibrium Slag Layer

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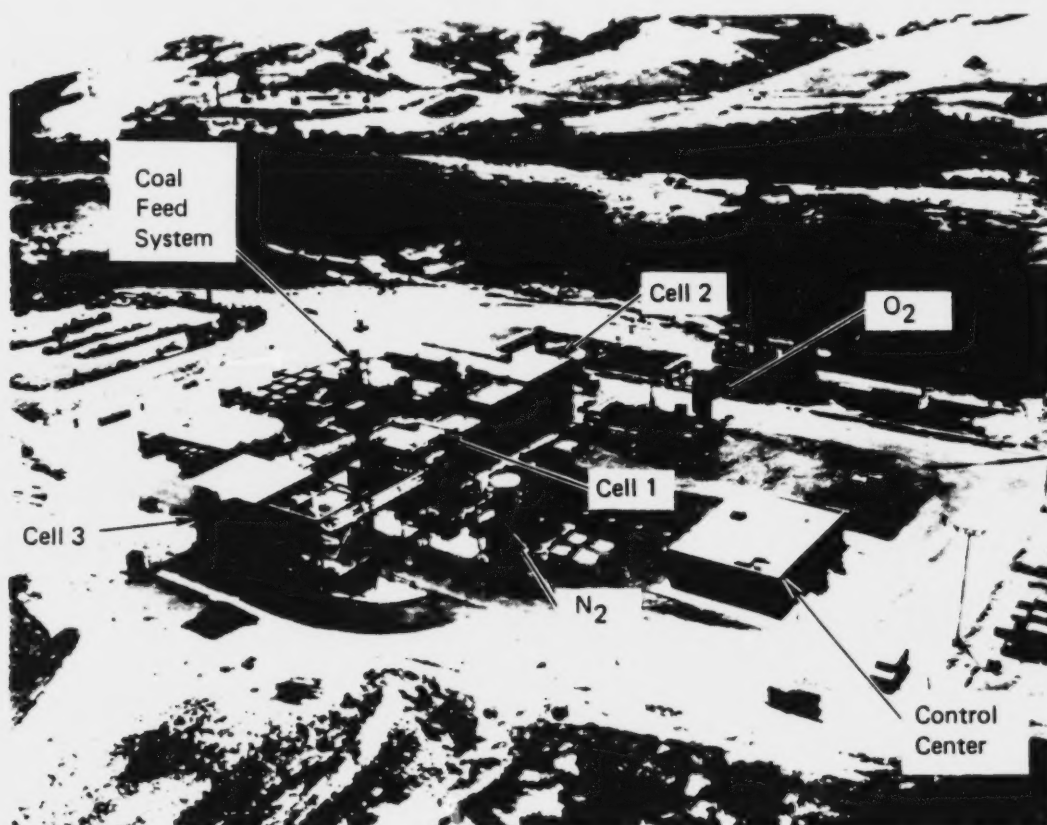


Figure 4. Fossil Energy Test Site (FETS)

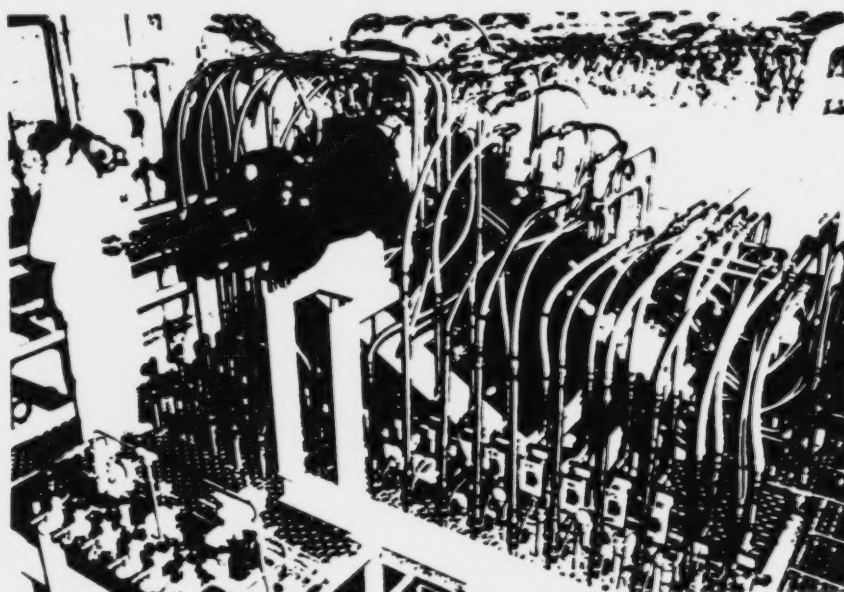


Figure 5. 10 MMBtu/Hr Commercial Test Unit

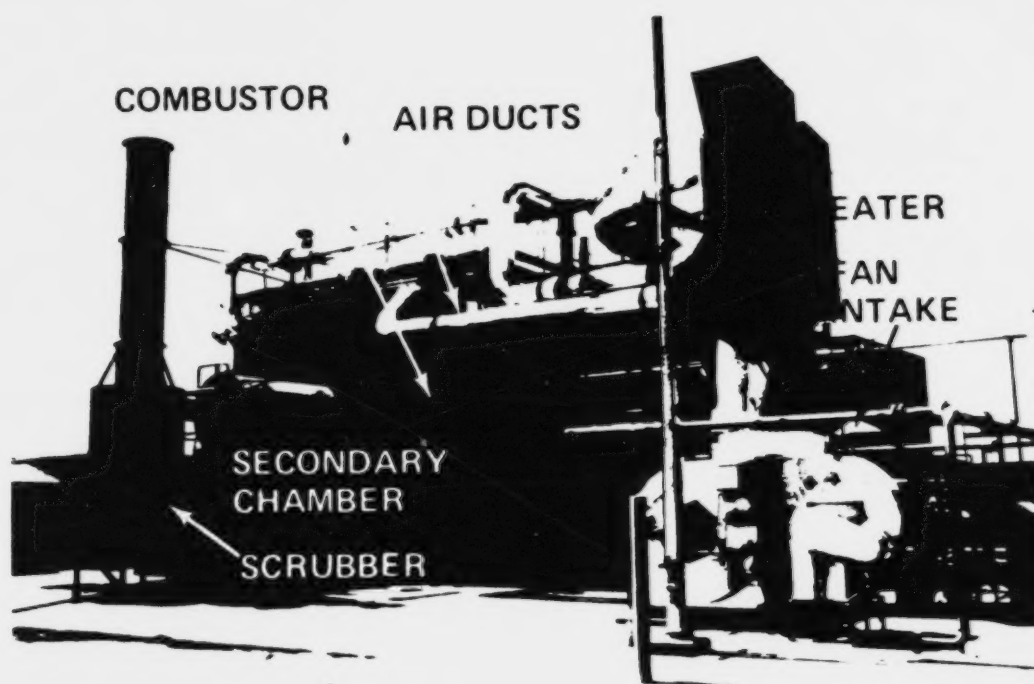


Figure 6. 10 MMBtu/Hr Coal Combustion Facility

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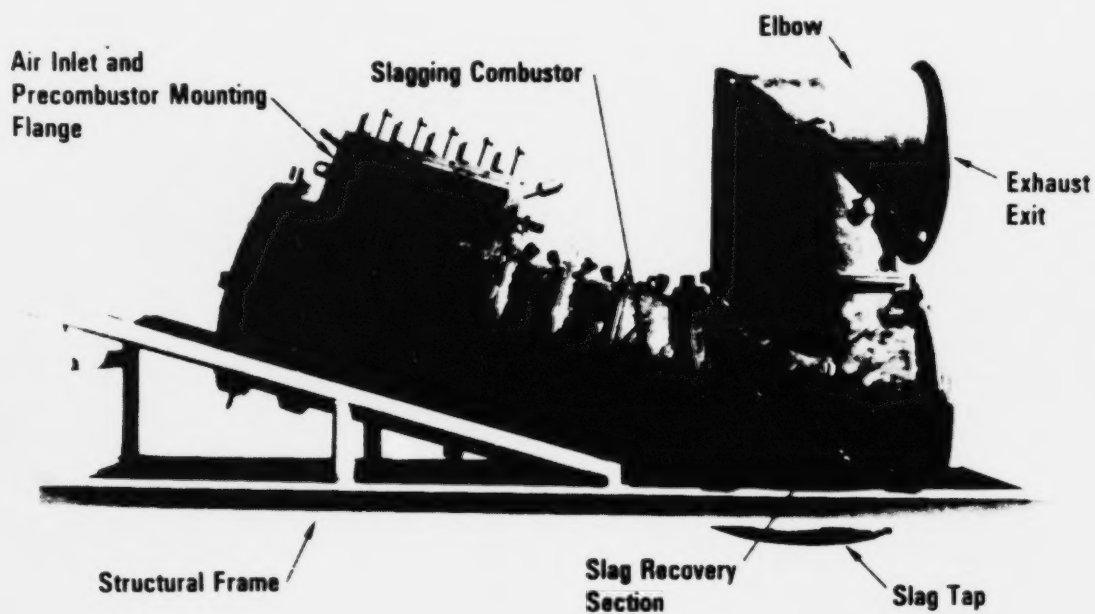


Figure 7. Scaled Commercial Test Unit (50 MMBtu/Hr) - Workhorse

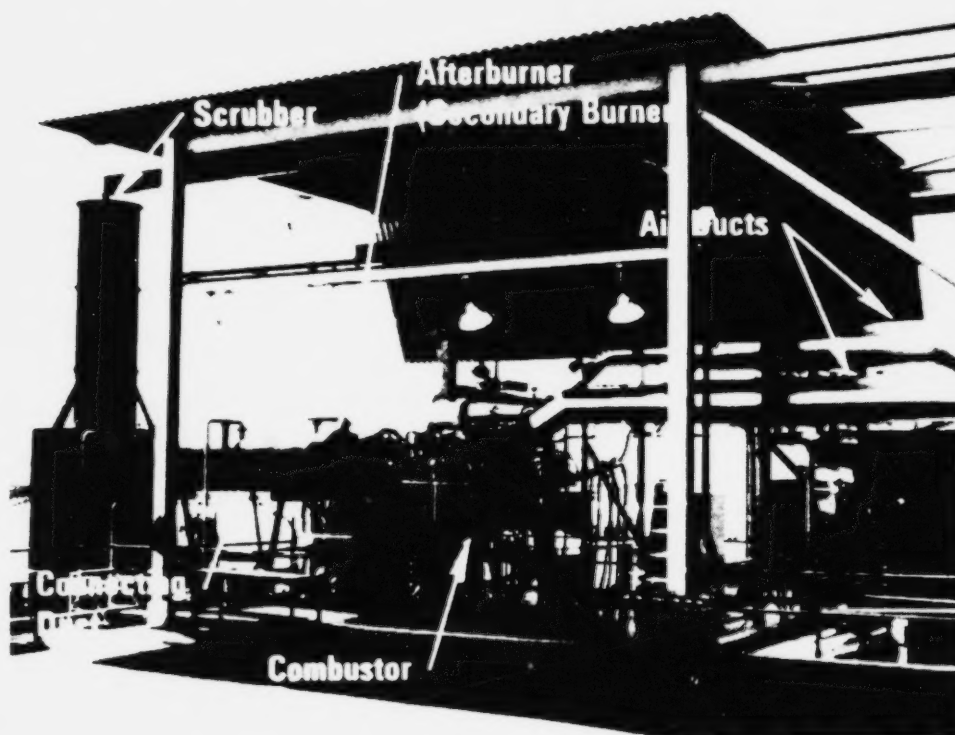


Figure 8. Overview of 50 MMBtu/Hr Combustor Test Set Up

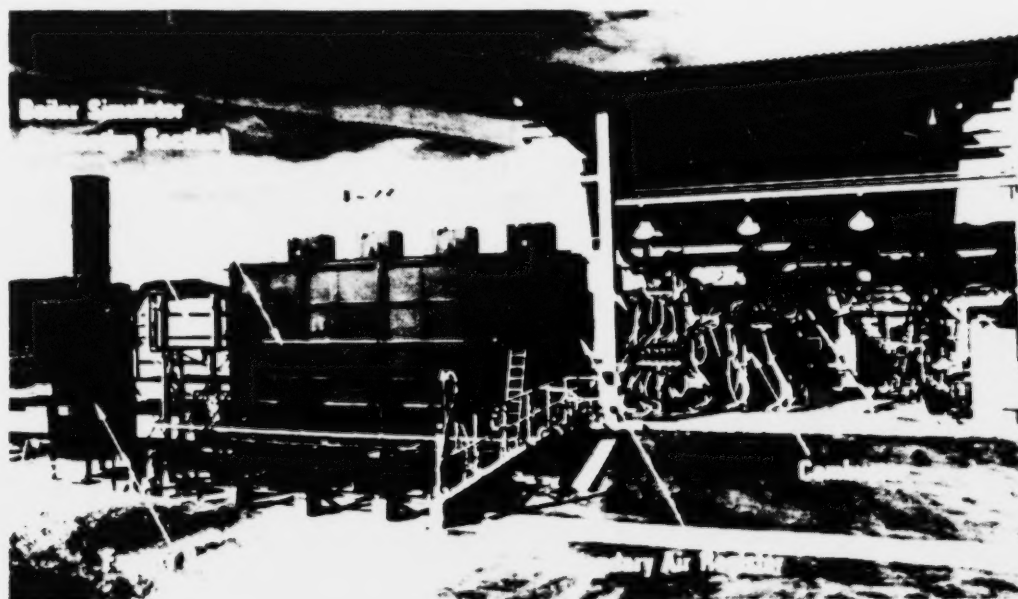


Figure 9. Overview of 50 MMBtu/Hr Combustor and Boiler Simulator

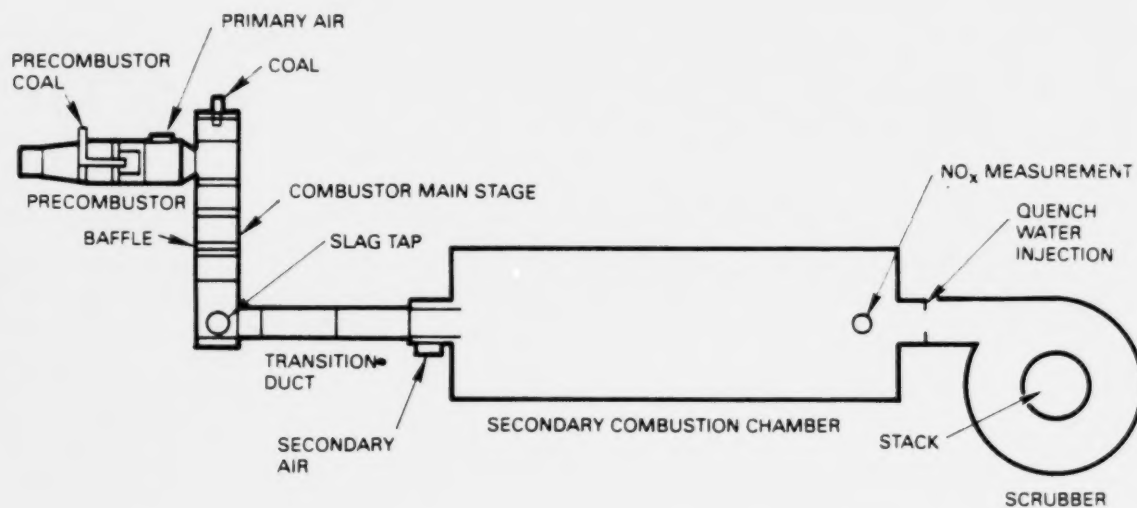


Figure 10. The 17-inch Atmospheric Slagging Coal Combustion System

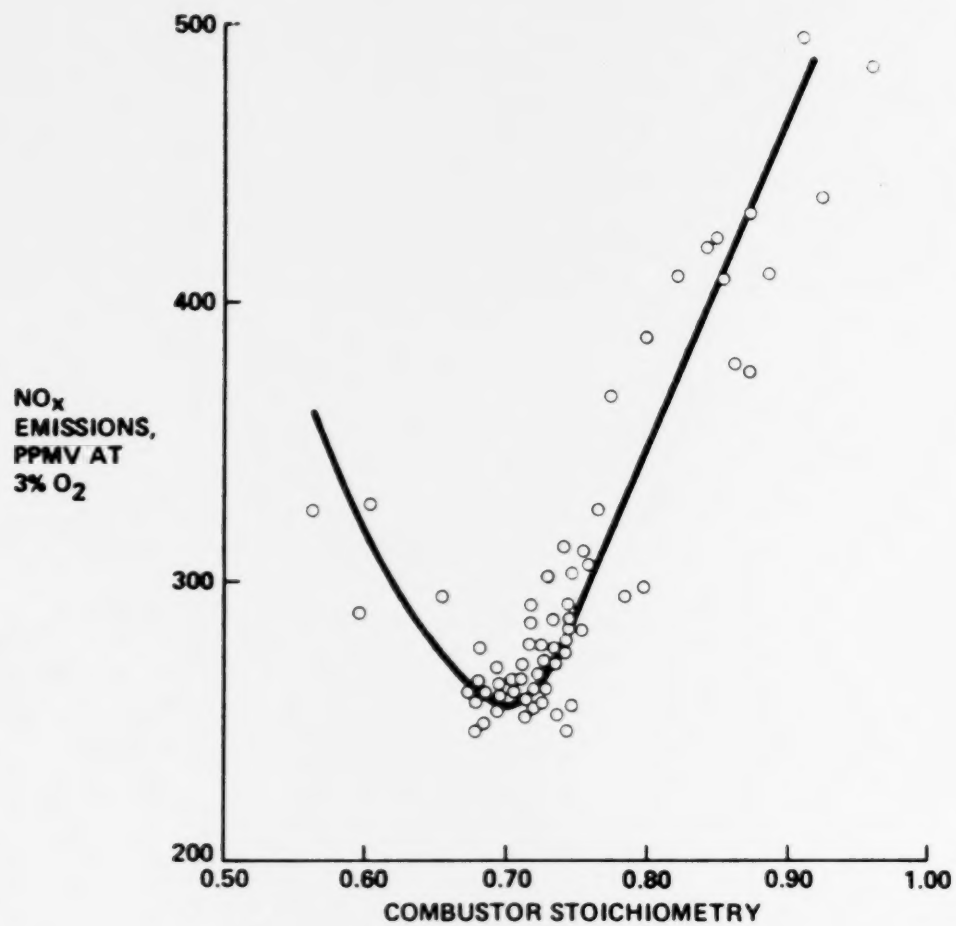


Figure 11. The Dependence of NO_x Emissions on Combustor Stoichiometry: All Utah Tests

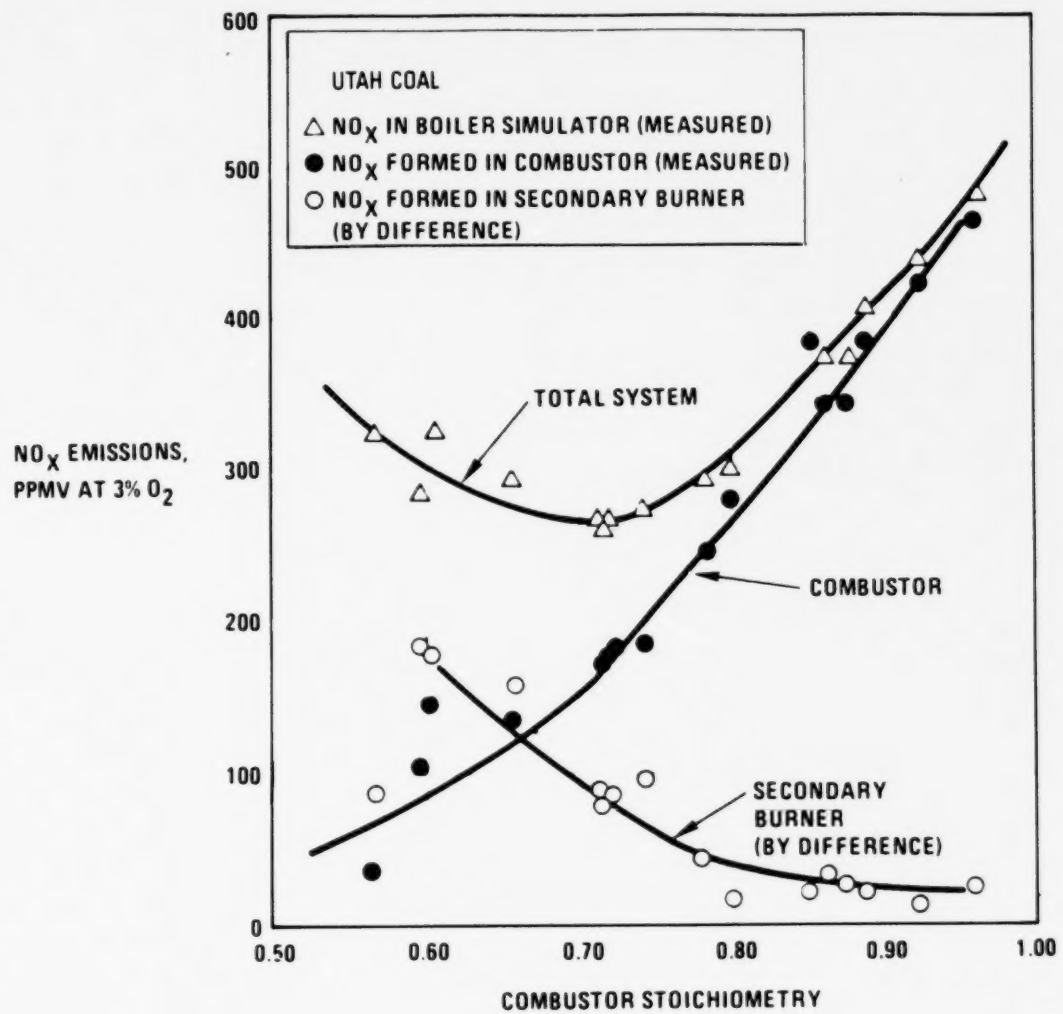


Figure 12. Total, Combustor, and Secondary Burner NO_x Emissions as a Function of Combustor Stoichiometry

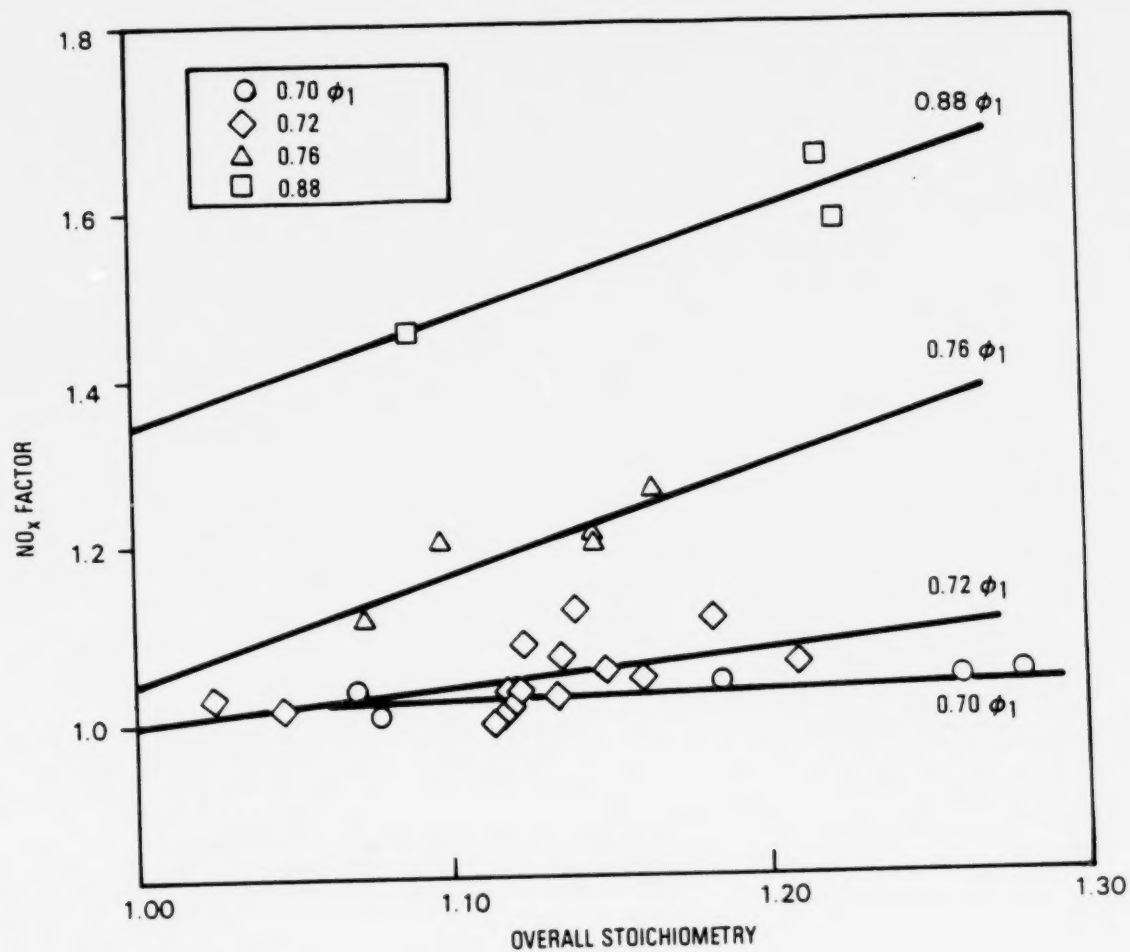


Figure 13. The Dependence of NO_x Emissions on Overall Stoichiometry at Constant Combustor ϕ for Utah Coal

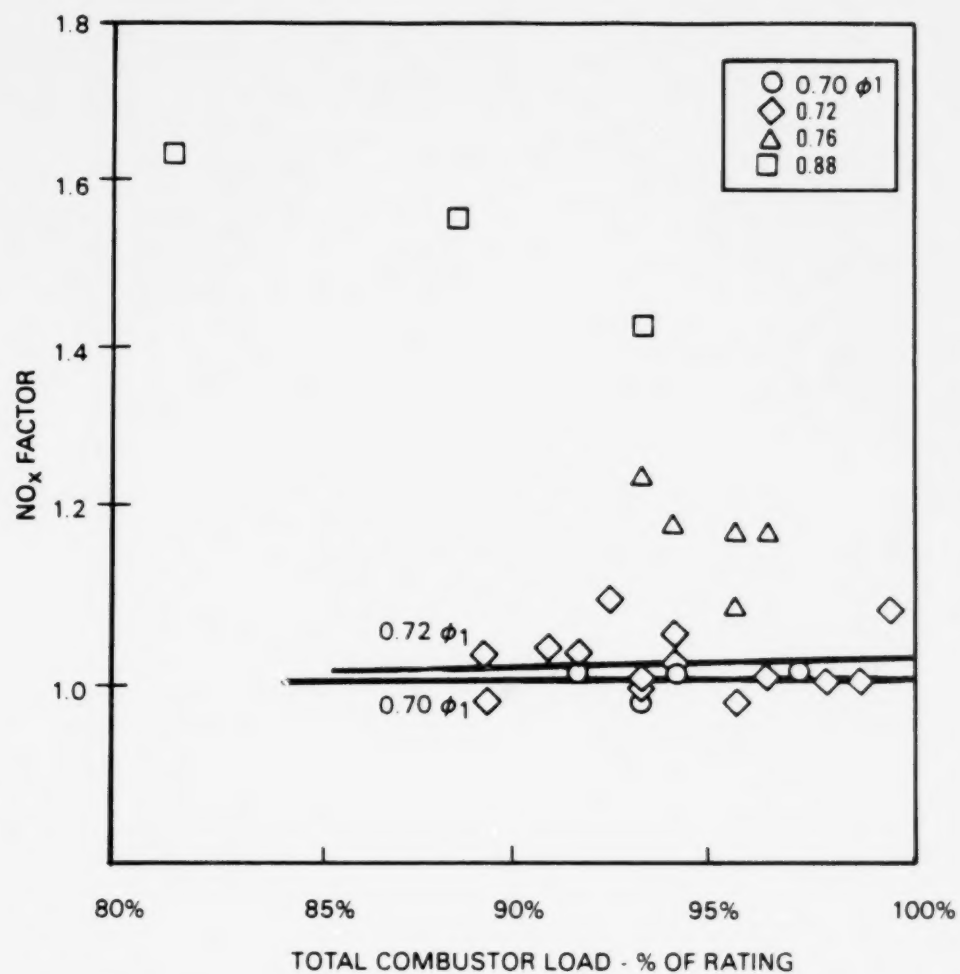


Figure 14. The Dependence of NO_x Emissions on Load at Constant Combustor ϕ When Firing Utah Coal

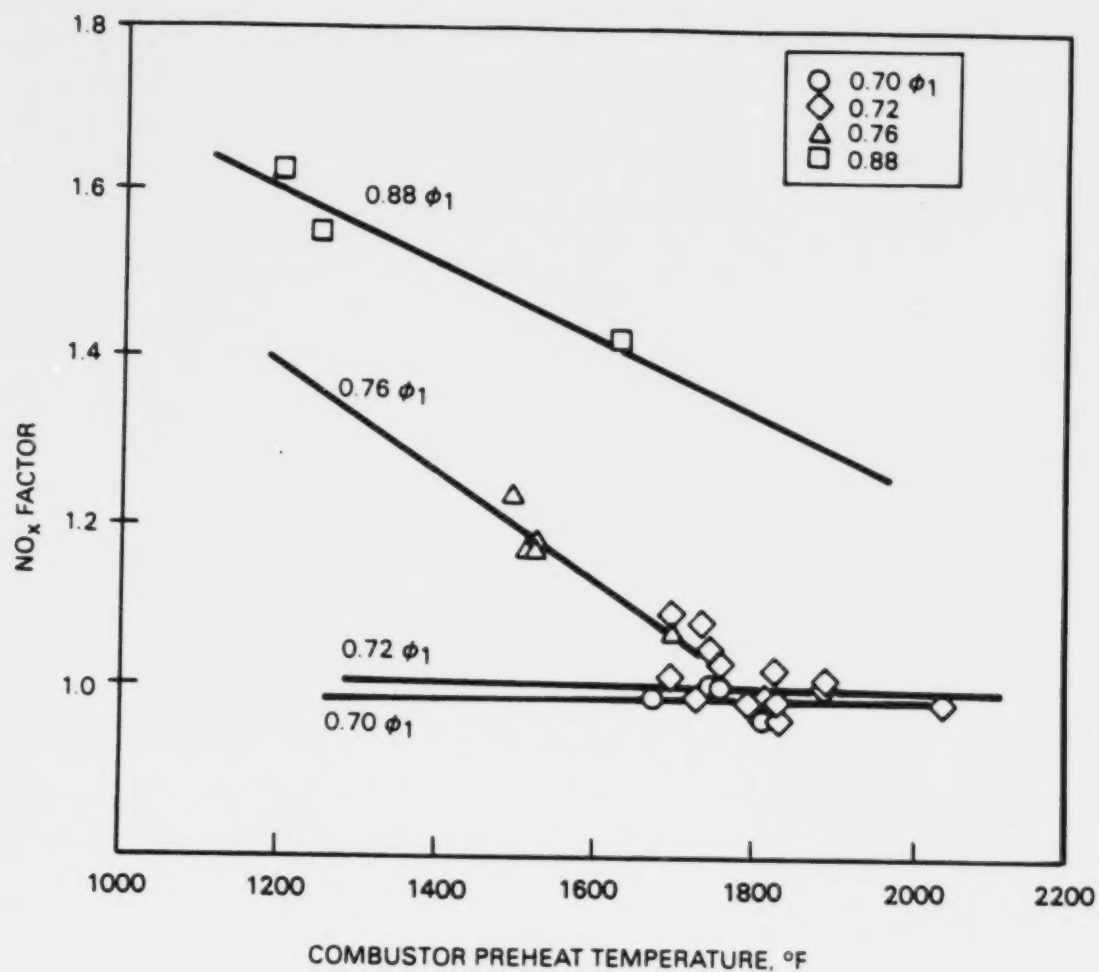


Figure 15 The Dependence of NO_x Emissions on Combustor Preheat at Constant Combustor ϕ for Utah Coal

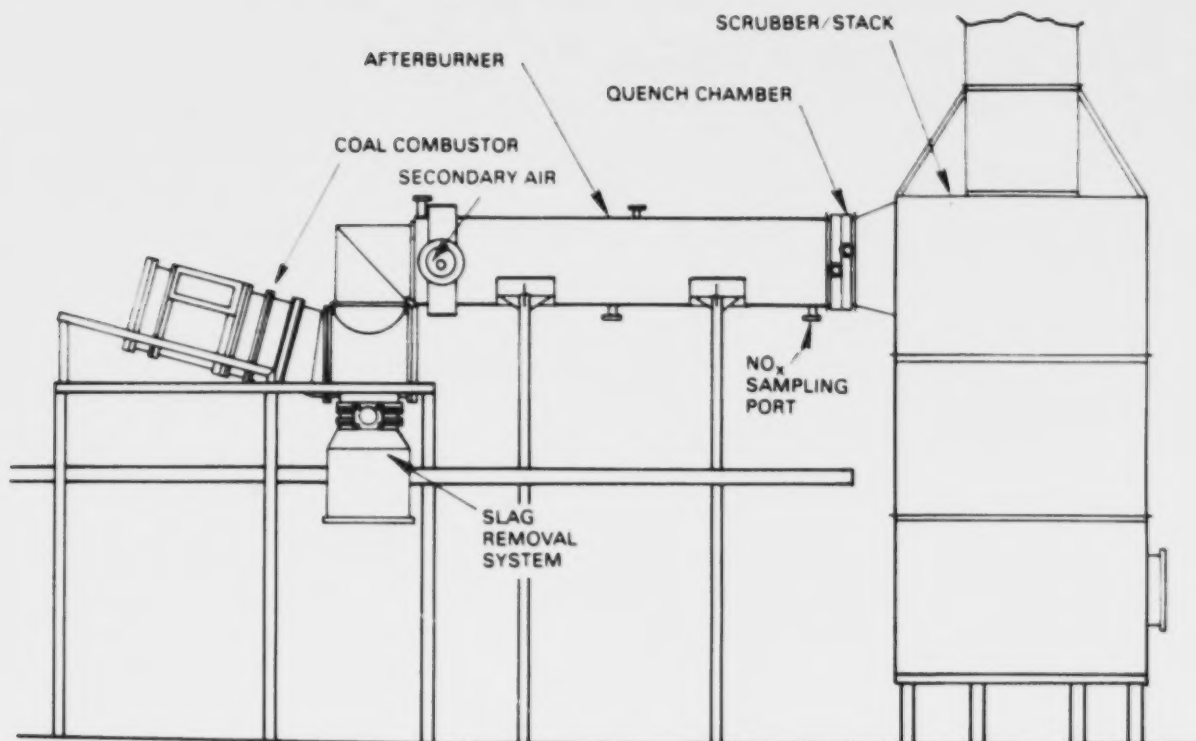


Figure 16 50 MMBtu/Hr Combustor Test System — Without Boiler Simulator

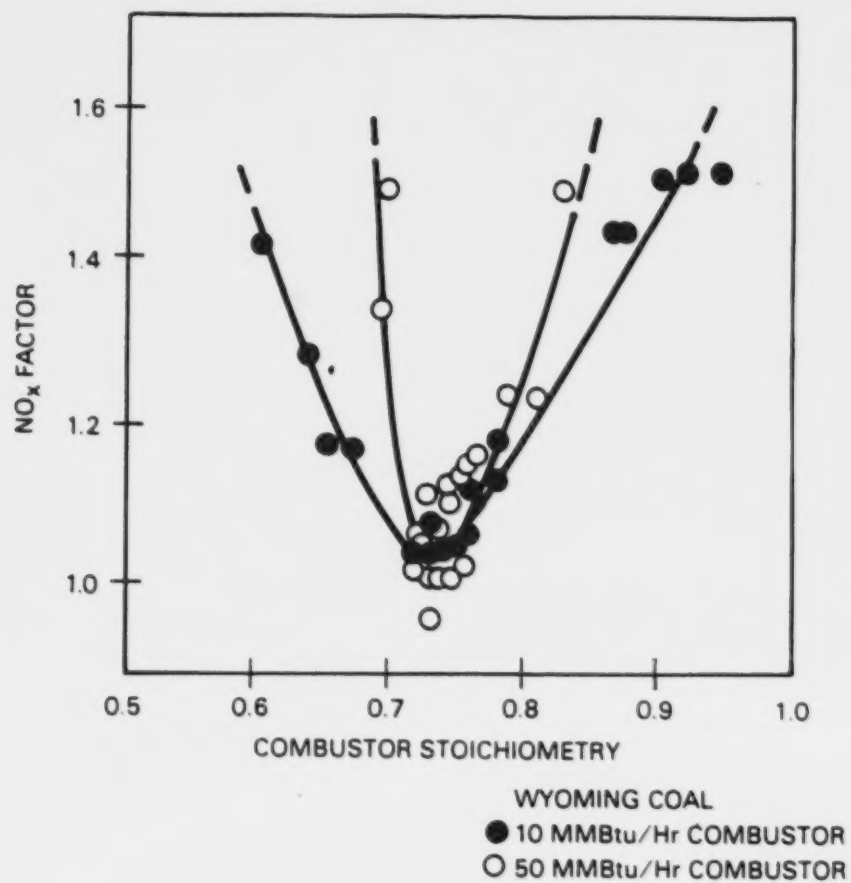


Figure 17 Data Comparison Between 10 MMBtu/Hr and 50 MMBtu/Hr Combustors

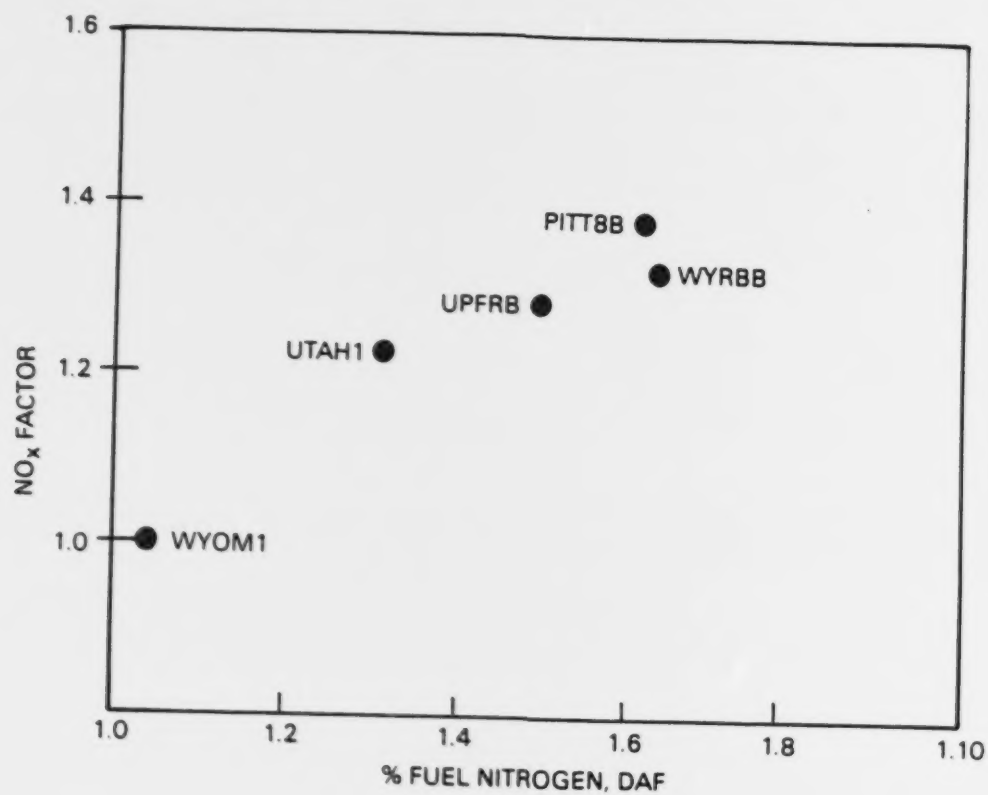


Figure 18 Effect of Fuel Nitrogen on NO_x Emissions — 50 MMBtu/Hr Combustor

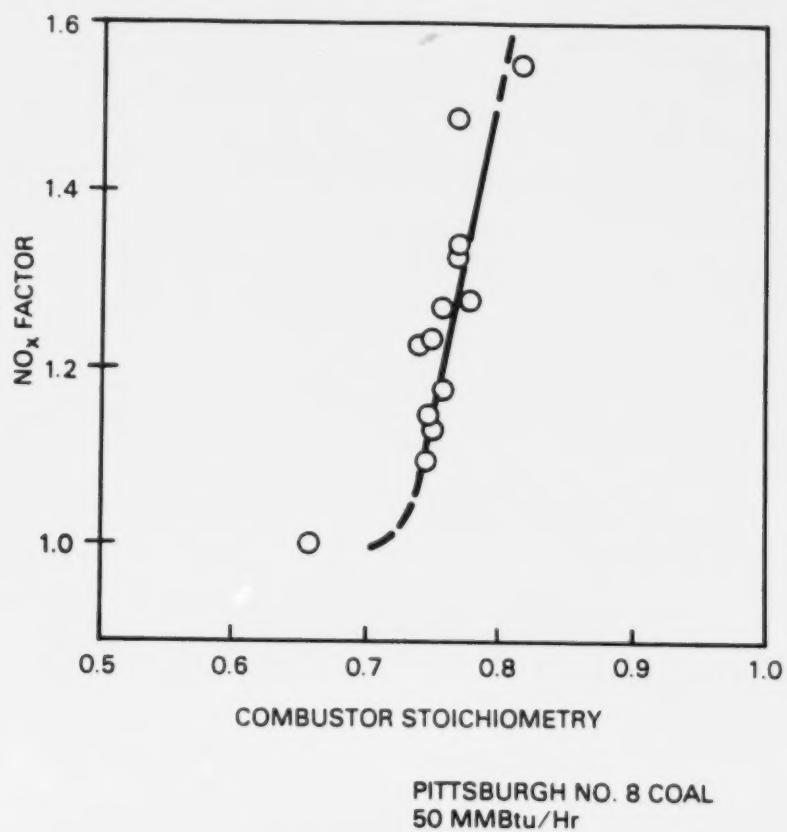


Figure 19 NO_x Variation with Stoichiometry in 50 MMBtu/Hr Combustor Without Boiler Simulator

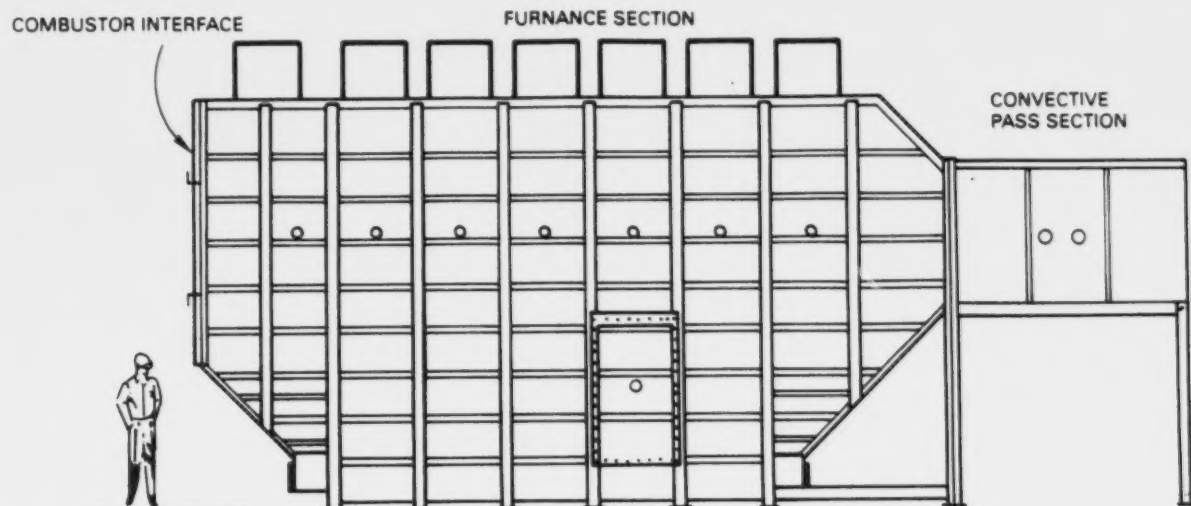


Figure 20 50 MMBtu/Hr Boiler Simulator

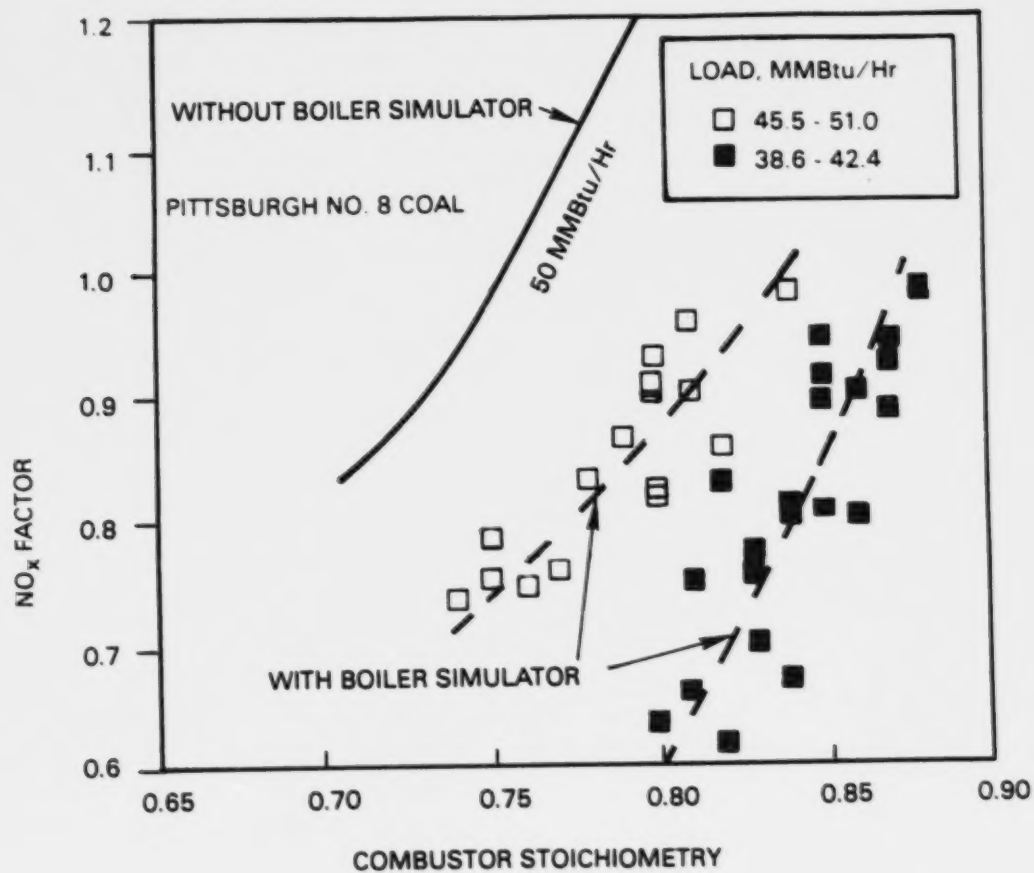


Figure 21 The Effect of Boiler Simulator on NO_x Emissions

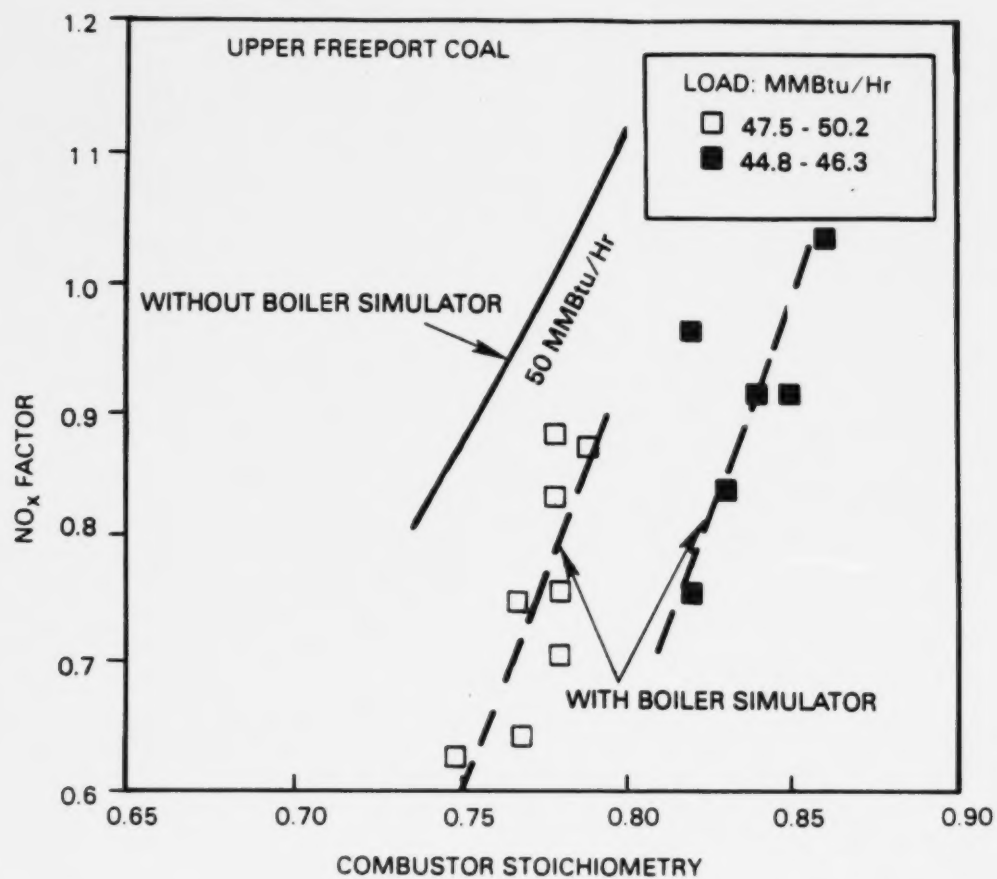


Figure 22 The Effect of Boiler Simulator on NO_x Emissions

Table I Analysis of Coals Fired in 10 MMBtu/Hr Combustor Tests

		<u>Utah Emergy</u>	<u>Wyoming Powder River Basin</u>	<u>Montana Rosebud</u>
Proximate Analysis				
Moisture	-	3.8	—	24.4
Volatiles	-	38.6	—	27.6
Fixed Carbon	-	49.7	—	36.0
Ash	-	7.8	—	11.9
HHV, Btu/lb		12,873	10,969	8,193
Sulfur	-	0.8	0.5	1.2
Ultimate Analysis				
Moisture	-	3.8	7.3	24.4
C	-	72.5	64.5	48.4
H	-	5.0	4.4	3.1
N	-	1.0	0.9	0.7
S	-	0.8	0.5	1.2
Ash	-	7.8	6.2	11.9
O	-	9.0	16.3	10.2

Table II Coals Tested in 50 MMBtu/Hr Combustor

Number	Coal Type	Moisture %	Ash %	Volatiles %	Nitrogen %	Sulfur %	HHV Btu/lb	T ₂₅₀ °F
1	Ohio No. 6 - Lot A	3.64	8.37	35.0	1.38	1.78	13,091	2460
	Ohio No. 6 - lot B	2.76	8.53	37.8	1.48	1.85	12,932	2547
	Ohio No. 6 - Lot C	3.66	7.27	34.9	1.50	1.54	13,291	2437
2	Wyoming - 1	7.25	6.18	—	0.90	0.47	10,969	2215
	Wyoming - B	7.77	6.64	40.1	1.40	0.71	11,736	2284
3	Pittsburgh No. 8	2.34	10.1	37.7	1.41	2.57	12,975	2475
4	Upper Freeport - Lot A	3.19	11.99	32.9	1.31	1.75	12,948	2565
	Upper Freeport - Lot B	2.71	10.24	33.4	1.30	1.89	13,157	2490
	Upper Freeport CWS	31.45	6.43	22.1	1.13	1.10	9,319	2550

Table III Summary Test Results

Power Level (MMBtu/Hr)	10-12	40-50
Diameter, I.D. (in.)	17	34
Length, (in.)	48	62
Air Preheat Temp. (°F)	400-700	100-500
Equivalence Ratio Range - 1st Stage	0.7-0.9	0.7-0.9
Max. Slag Capture (%)	91	94
Carbon Burnout (%)	>99.5	>99.5
NO _x - (PPM)	230-450	230-450
Outlet Temp. (°F)	2800-3200	2800-3200
Total No. of Firings	375	196
Individual Runs (Hr.)	1-8	1-2

METHANOL DUAL-FUEL COMBUSTION

by

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ABSTRACT

Dual-fuel combustion is a technique invented to lower emissions of NO_x from boilers. This paper presents experimental data using this technique in a utility boiler at a level of 35 megawatts. Tests with low sulfur (0.21% S) oil/natural gas, low sulfur oil/methanol, and natural gas/methanol were performed, and the NO_x emissions data were compared with NO_x emissions of 100% low sulfur oil, gas, and methanol.

Tests with a mixture of 70% natural gas/30% methanol revealed that the NO_x emissions level using the dual-fuel technique was lower than those obtained with either 100% gas or 100% methanol. The NO_x level was about 25% of the level obtained with natural gas fired in a conventional combustion mode or about 50% of the NO_x level obtained with natural gas fired in a "staged" combustion or "burners out-of-service" mode, a state-of-the-art combustion modification technique used to lower NO_x emissions.

DUAL FUEL METHANOL COMBUSTION

INTRODUCTION

One combustion modification technique used to reduce the amount of NO_x emitted in the boiler is known as a dual-fuel combustion process. This was discovered by Jones and Mansour^{1,2} during experiments in a 45 MW boiler at Southern California Edison's (SCE) Highgrove Generating Station with shale oil combustion. By burning a fuel oil which contained less nitrogen in the top row of burners over a shale oil containing a larger amount of nitrogen being combusted in the lower row of burners, NO_x emissions were lower than the NO_x emissions from burning a blend of the two oils. Later work performed by Radak,³ et al., with natural gas and low sulfur fuel oil in a larger boiler (175 MW) at SCE's Alamitos Generating Station confirmed the dual-fuel technique as a method in which lower amounts of NO_x could be obtained using this process compared to burning either of the pure fuels alone. During boiler tests (45 MW) in 1981 at the Highgrove Generating Station with pure methanol (Weir,⁴ et al.), a few experiments were performed with simultaneous combustion of methanol and gas in separate burners. E. A. Danko⁵ obtained a patent on the use of methanol and natural gas in the dual-fuel mode based on these experiments. Until the current work was performed, however, no test had been made of the dual-fuel concept with oil and methanol. These experiments, therefore, report the first use of methanol and oil in the dual-fuel mode and much more extensive experiments with methanol and natural gas in the dual-fuel mode.

Southern California Edison's Highgrove Generating Station Unit 4 is located in Grand Terrace, California, in San Bernardino County and was constructed in 1955. Highgrove Unit 4 is a drum type non-reheat boiler with a total of six burners in two rows as shown in Figure 1. The boiler is rated at 45 MW_e and was manufactured by Combustion Engineering. The burners used in the test program were Babcock and Wilcox "Racer" burners previously used in the 1981 pure methanol test. In the initial test of methanol combustion in a boiler in 1972 by New Orleans Public Service, and others, the use of burners not designed for methanol combustion resulted in many problems.

Modifications to the generating station necessary for methanol combustion were previously described.⁴ The same storage tank and the same rail car unloading facility used in the 1981 experiments were reused. The methanol pump was re-sized to permit accurate delivery of lower amounts of methanol. Consequently, maximum load capability on 100% methanol input was limited to 22 MW. Commercial methanol was supplied in four rail tank cars by Celanese Chemical Corporation. The higher heating value ranged from 9,390 to 9,500 Btu per lb. (21841 kJ/kg - 22097 kJ/kg).

DESCRIPTION OF EXPERIMENTS

1. BASELINE TESTS

Figure 1 is a sketch of the burner arrangement. In the data shown in Figure 2, the same fuel was combusted in all six burners.

Figure 2 presents NO_x emission data as a function of load for natural gas, low sulfur (0.21% S) oil, and methanol. The data points above 35 MW were obtained from Weir, et al.,⁴ in 1981 on the same boiler. The remainder of the experiments presented in this paper were performed at 35 MW. The 35 MW load was selected so that a wide range of fuel mixture ratios could be used. For example, it would be extremely difficult, if not impossible, to provide 80% of the fuel needed to generate 45 MW through only Burners 4, 5, and 6 (Figure 1).

2. "STAGED" COMBUSTION TESTS

Figure 3 shows the effect on NO_x emissions of "staging" with all gas fuel. By taking the No. 2 burner out-of-service (i.e., "staging") NO_x emissions are lowered in the case of gas by almost 50%.

Figure 4 shows the same type of "staged" combustion with low sulfur oil; however, the NO_x reduction in emissions is not as great as with gas.

In Figure 5, data is presented on three fuel combinations in the "staged" combustion mode - oil with No. 2 burner out-of-service, gas with No. 2 burner out-of-service, and a single point with a mixture of 70% gas and 30% methanol with the No. 2 burner out-of-service. In this latter experiment, methanol was fired in Burners 1 and 3 and gas in Burners 4, 5 and 6. Thus, while removing the No. 2 burner from service provides a reduction of about 50% in NO_x emissions with all gas fuel, the methanol over gas dual-fuel mode results in a further 50% reduction in emissions when the overall thermal input due to methanol was 30%. It should be noted, however, that there is a difference in burner equivalence ratio (i.e., stoichiometry) between the latter two cases.

3. DUAL-FUEL COMBUSTION TESTS

Figure 6 presents a comparison in which low sulfur oil is provided to Burners 4, 5 and 6 in both series of tests. In one case, gas is provided to Burners 1, 2 and 3 whereas in the second case methanol is provided to Burners 1, 2 and 3. The two curves cross over at about 70% oil thermal input.

The upper curve in Figure 7 presents the case in which methanol is fired in Burners 1, 2 and 3 and oil in the lower row of Burners 4, 5 and 6 (this curve uses the same data as the second case shown on the previous graph). In the lower curve, methanol is fired in Burners 1, 2 and 3 and natural gas in Burners 4, 5 and 6. It is important to note in both Figures 6 and 7 that by definition, a change in the percentage of fuel in both burner elevations results in a change of burner equivalence ratio for both burner elevations. This occurs because air flow to each burner remains constant.

STOICHIOMETRY IN DUAL-FUEL COMBUSTION TESTS

The symbol ϕ (or equivalence ratio) is frequently used to indicate the stoichiometry in combustion tests and is particularly convenient when different fuels are used since the absolute fuel/air ratio would be different at the stoichiometric point for each fuel. In this paper, ϕ is defined as the actual fuel/air ratio by weight divided by the stoichiometric or theoretical fuel/air ratio for that fuel. Thus, values of ϕ greater than 1.0 are fuel-rich while values of ϕ less than 1.0 are fuel-lean. (The assumption was made in calculating equivalence ratio that the air in the windbox was evenly distributed among the six burners.)

Figure 8 presents NO_x as a function of the equivalence ratio in the lower burners for various dual-fuel combinations. This illustrates the benefit of the fuel-rich combustion in the lower burner elevation and clearly indicates that methanol over gas allows lower NO_x emissions than methanol over oil or gas over oil. It was observed, at an equivalence ratio approaching 1.4 (corresponding to 20% thermal methanol input), that some difficulties were experienced with flame stability (this might not be true in larger boilers), but a satisfactory flame was obtained at an equivalence ratio of 1.3 (approximately 30% methanol input).

Figure 9 depicts in bar graph form, the benefits of dual-fuel combustion compared to gas and oil firing--both staged and unstaged.

DISCUSSION

The methanol dual-fuel process derives its NO_x reduction capability as the result of three factors. The first factor is that methanol contains no fuel bound nitrogen and, hence, no NO_x is formed from this source as in other conventional utility liquid fuels. The second factor is that the theoretical flame temperature is less than natural gas or fuel oil, thus less NO_x is formed by dissociation or the Zeldovich effect. The third factor is that fuel rich combustion of the primary fuel (natural gas or oil) results in less NO_x . It is well documented that fuel-rich combustion results in the formation of less thermal and fuel NO_x . The practical application of this process in a furnace (i.e., fuel rich combustion) is limited by the formation of partial oxidation products (CO) or soot (carbon or heavy hydrocarbons) resulting from incomplete combustion. Methanol allows fuel-lean combustion in the upper burner elevation providing vitiated air to complete the primary stage (gas or oil) fuel-rich combustion without producing substantial NO_x itself.

In the dual-fuel experiments, the thermal input due to methanol ranged from 20% to 55%. However, by comparison to 100% gas or 100% oil, it is possible to see the benefit in NO_x reduction obtained by substituting a little methanol for oil or gas in the top three burners. With oil, substituting 20% to 30% methanol, results in reducing the NO_x from 185 ppm to around 120 ppm (a 35% reduction). In an all gas-fired boiler, with all burners in service where the NO_x emissions level is around 215 ppm, substitution of methanol in the top three burners lowers the NO_x emissions level to slightly under 40 ppm. This is a little more than 80% reduction compared to gas being fired with all burners in service or about 50% of the level when the top center (No. 2 burner) is taken out-of-service (See Figure 5).

Figure 7 also indicates that substitution of 20%-40% methanol (as determined by fuel heating value input) in an all gas flame results in NO_x

emission levels which are lower than either 100% gas or 100% methanol without staging.

Since methanol, being normally produced from natural gas, is generally more expensive than natural gas, the desire to minimize the amount of methanol required to obtain significant NO_x reductions is evident. Thus, while the data indicates that 20% methanol would serve this purpose, flame stability and other operating problems dictate that 30% methanol should be the minimum amount of methanol substituted. This applies to the 45 MW boiler with only two rows of burners. It is quite possible that with larger boilers the minimum methanol input may be lower.

Figure 6 compares the effect of substituting either methanol or natural gas in the upper row of burners in an oil-fired boiler. There does not appear to be any significant difference whether natural gas or methanol is substituted for 15% to 35% of the oil being burned. Both cases result in around 40% NO_x reduction compared to 100% oil. For smaller thermal inputs of oil substitution, methanol is superior to gas substitution. The reason for the relatively flat NO_x curve with methanol over oil is not known.

The scenario for methanol use then is governed by fuel price and availability together with the need, if any, for NO_x reduction by the boiler operator. Referring again to Figure 6, one might say that since natural gas is cheaper than methanol, substitution of natural gas for 30% of the oil to achieve a 40% NO_x reduction would be the most economical path. However, one might question the likelihood of a situation in which 30%, but not 100%, of natural gas would be available for utility use at a single boiler. It would be possible, however, that methanol, a storable fuel, would be available when natural gas is not. In that case, a 30% methanol/70% oil use would result in a NO_x emission level of about 115 ppm, much lower than with 100 percent oil used in the normal manner. This level (115 ppm) is also lower than could be obtained by "staging" (taking No. 2 burner out-of-service) a 100% oil flame.

If natural gas, which may or may not be a cheaper fuel than low sulfur oil, were available, the substitution of 30% methanol results in greater NO_x reductions than could be obtained by "staging" the all gas flame.

One experiment was also performed with 100% methanol at a 20.5 MW load and No. 2 burner out-of-service. This resulted in a NO_x level of 32 ppm compared to NO_x levels of 43 to 57 ppm with no burners out of service at 20 to 21.5 MW. Thus staging of pure methanol allows a reduction in NO_x levels in addition to the reduction obtained by fuel switching (oil or gas to methanol).

FUTURE PLANS

As shown in Figure 1, the boiler used in these tests had only two rows of burners, three burners in each row. The tests were thus limited, since only one burner could be taken out of service and, as stated previously, there were limitations in how much conventional fuel could be "forced" through the lower three burners. To avoid these limitations, another set of dual-fuel tests with methanol are planned to be concluded during 1987 on a 215 MW boiler at SCE's Huntington Beach Generating Station. This boiler has four rows of burners, six burners per row so that some of the limitations of tests reported in this paper will be avoided. The tests are planned to be jointly sponsored by Celanese Corporation and Southern California Edison Company.

CONCLUSION

It is concluded that:

1. Substitution of methanol for 30% of natural gas (as measured by fuel heating value) results in NO_x emission levels considerably lower than either all gas, gas with a "burner out-of-service", or all methanol flames.
2. Substitution of methanol for 30% of the oil (as measured by fuel heating value) results in NO_x emissions levels lower than with a 100% oil flame, even if "staged". This option could be exercised if natural gas were not available but methanol, a storable fuel, was available and NO_x emissions levels were desired to be reduced.
3. Creating two discrete combustion stages within the boiler and selecting the combustion stoichiometry and fuel-type in each stage are key factors contributing to the NO_x reduction achieved by the process.
4. The NO_x reduction achieved by the dual-fuel process is the result of three factors: (1) Control of NO_x formation through the optimum use of fuel-rich combustion in the lower burner elevation, (2) Control of NO_x formation with the use of a nitrogen free fuel in the upper burner elevation, and (3) use of a fuel with a lower flame temperature.
5. There are no significant operating problems resulting from the use of dual-fuel methanol combustion when the local burner equivalence ratio does not exceed 1.4. At richer mixtures, burner stability problems may occur.

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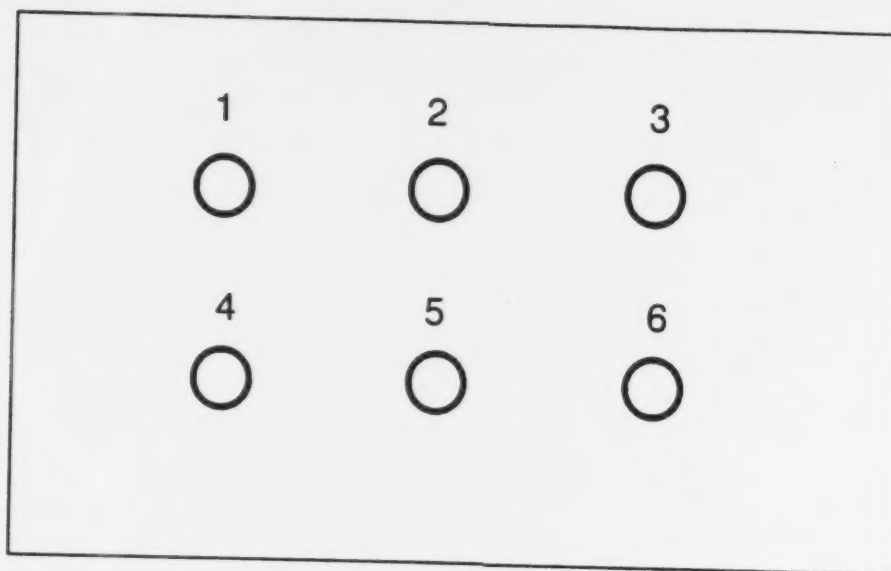


FIGURE 1: BURNER ARRANGEMENT - FRONT ELEVATION

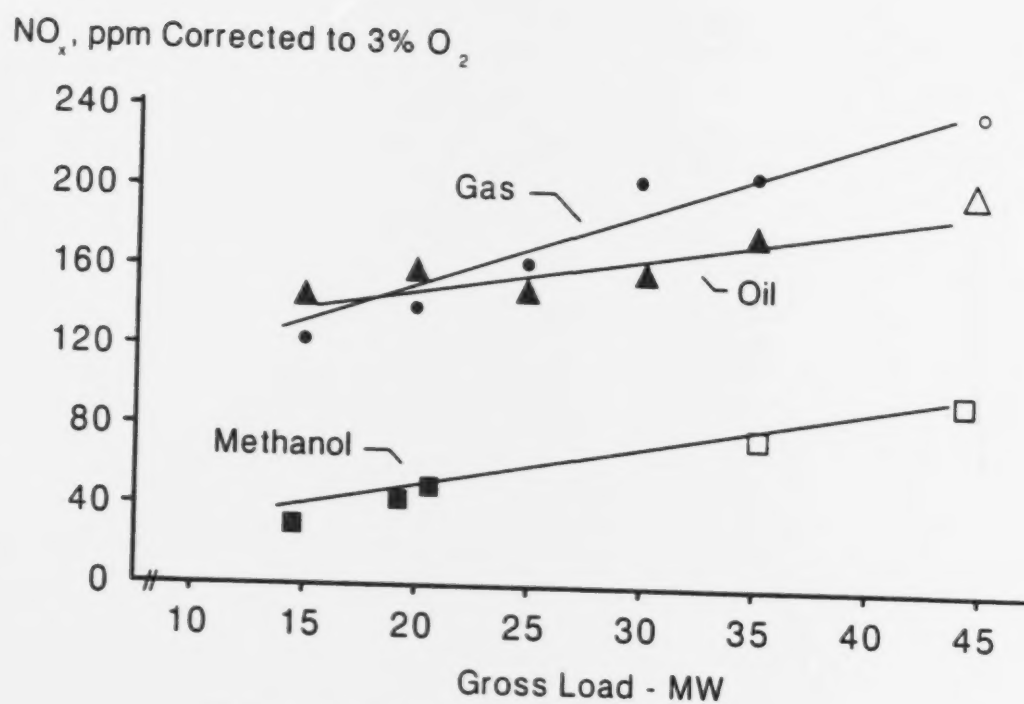


FIGURE 2: NO_x EMISSIONS AS A FUNCTION OF BOILER LOAD. ALL BURNERS ARE IN SERVICE. WHITE SYMBOLS REPRESENT DATA OBTAINED ON THE SAME BOILER IN 1981 (WEIR, ET AL.)⁴

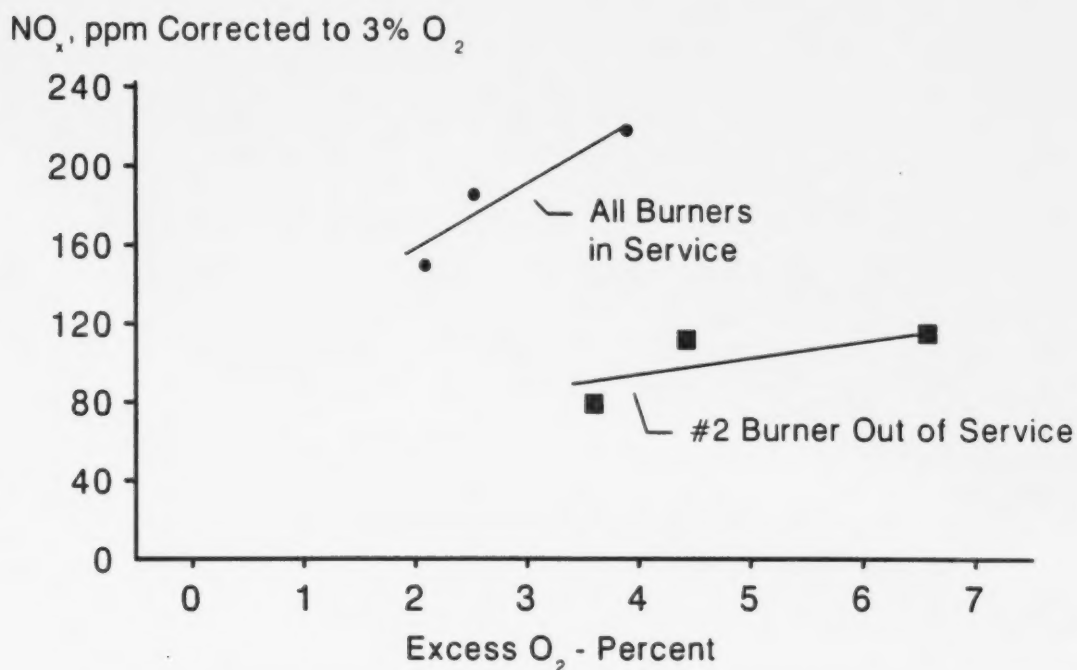


FIGURE 3: THE EFFECT OF "STAGING" WITH GAS FUEL AT 35 MW.

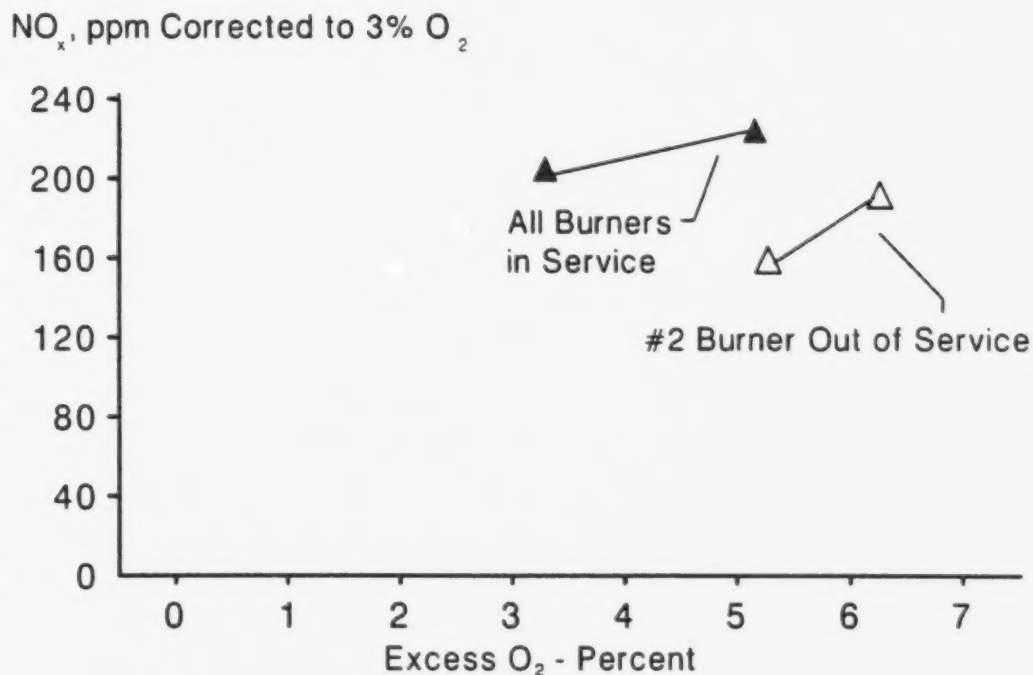


FIGURE 4: THE EFFECT OF "STAGING" WITH OIL FUEL AT 35 MW.

NO_x, ppm Corrected to 3% O₂

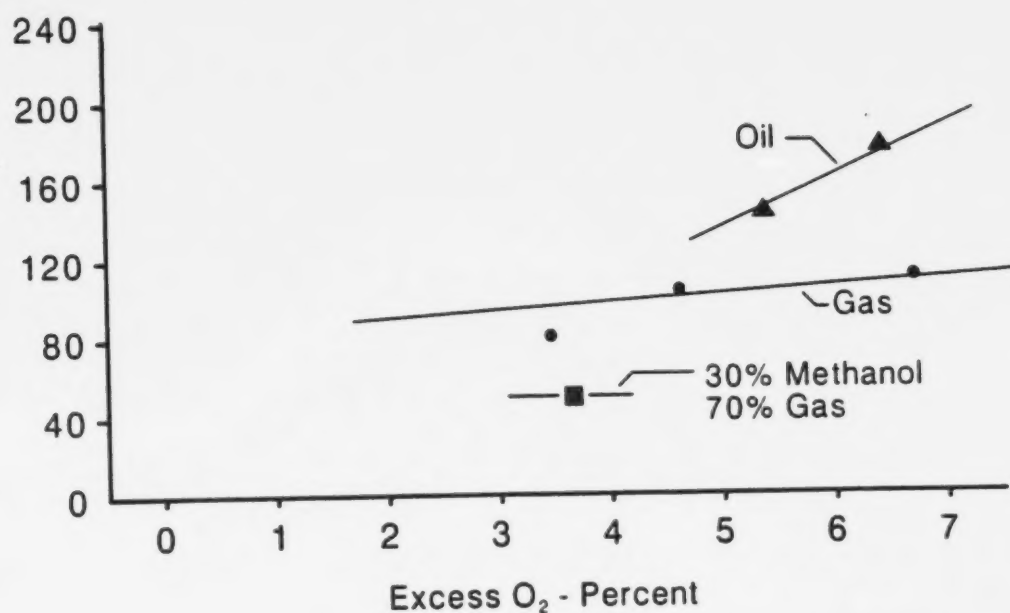


FIGURE 5: COMPARISON OF NO_x EMISSIONS WITH VARIOUS FUELS AND NO.2 BURNER OUT-OF-SERVICE AT 35 MW.

NO_x, ppm Corrected to 3% O₂

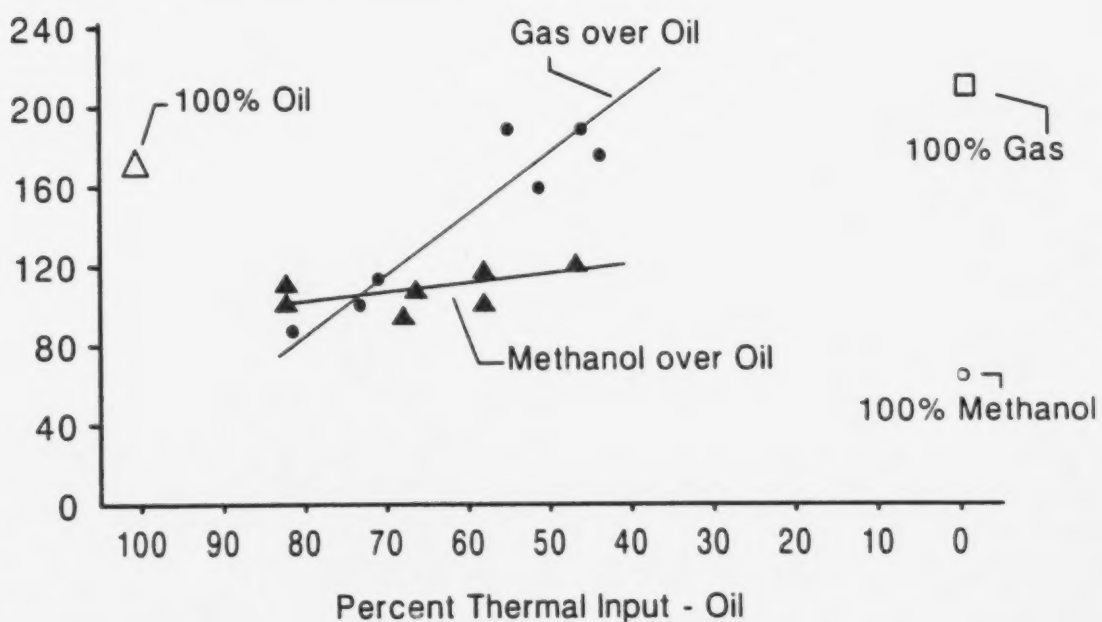


FIGURE 6: COMPARISON OF METHANOL AND GAS IN DUAL-FUEL COMBUSTION OIL AT 35 MW.

NO_x, ppm Corrected to 3% O₂

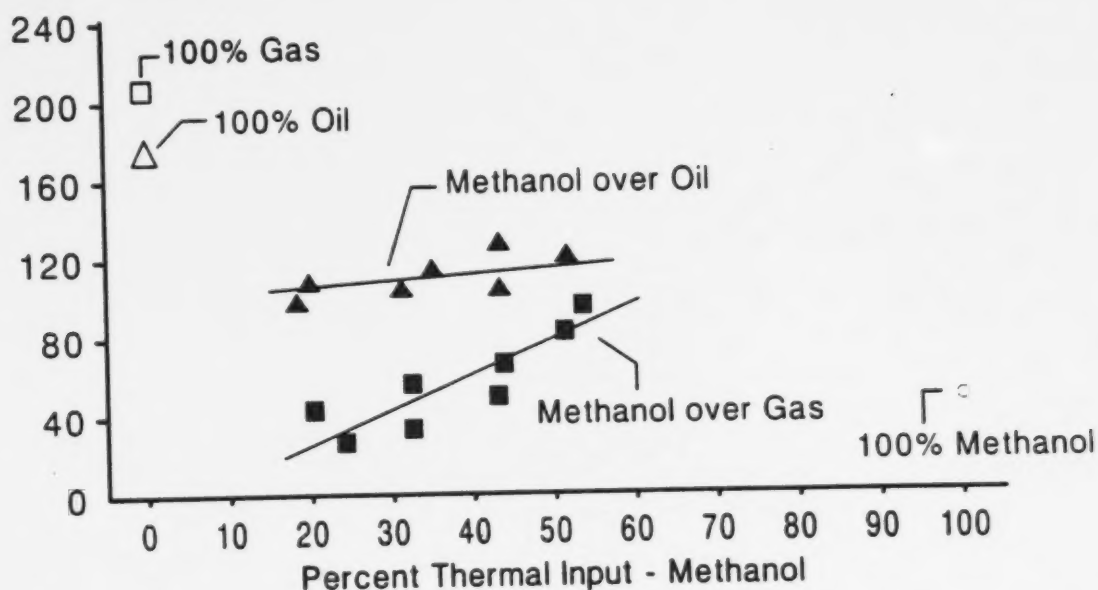


FIGURE 7: DUAL-FUEL COMBUSTION OF METHANOL WITH OIL AND WITH GAS AT 35 MW. DATA IN THE TOP CURVE WAS PREVIOUSLY PRESENTED IN THE LOWER CURVE IN FIGURE 6.

NO_x, ppm Corrected to 3% O₂

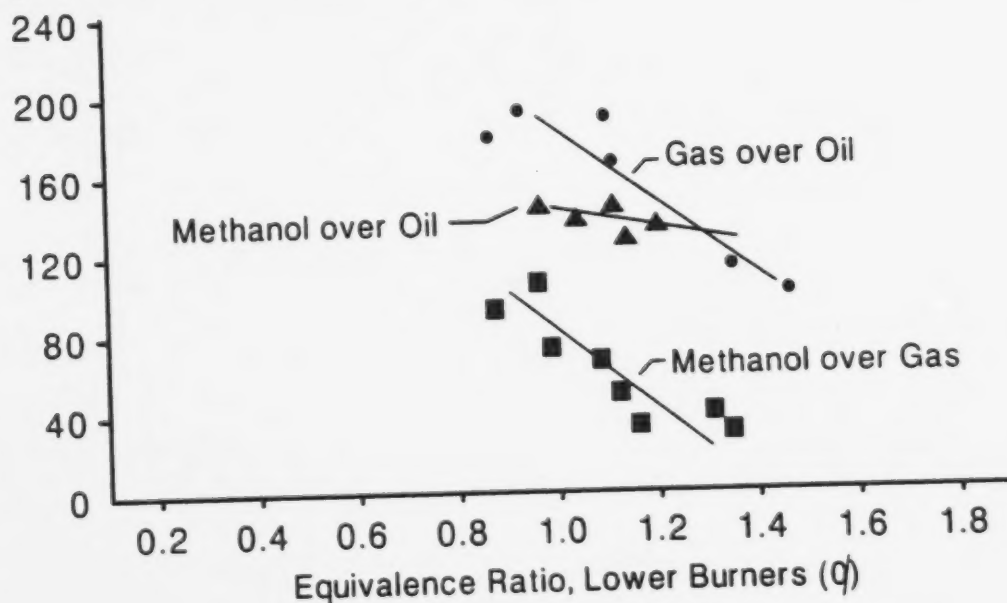


FIGURE 8: NO_x EMISSIONS VS. BURNER EQUIVALENCE RATIO WITH DUAL-FUEL COMBUSTION AT 35 MW. ALL BURNERS IN SERVICE.

NOx PPM Corrected to 3% O₂

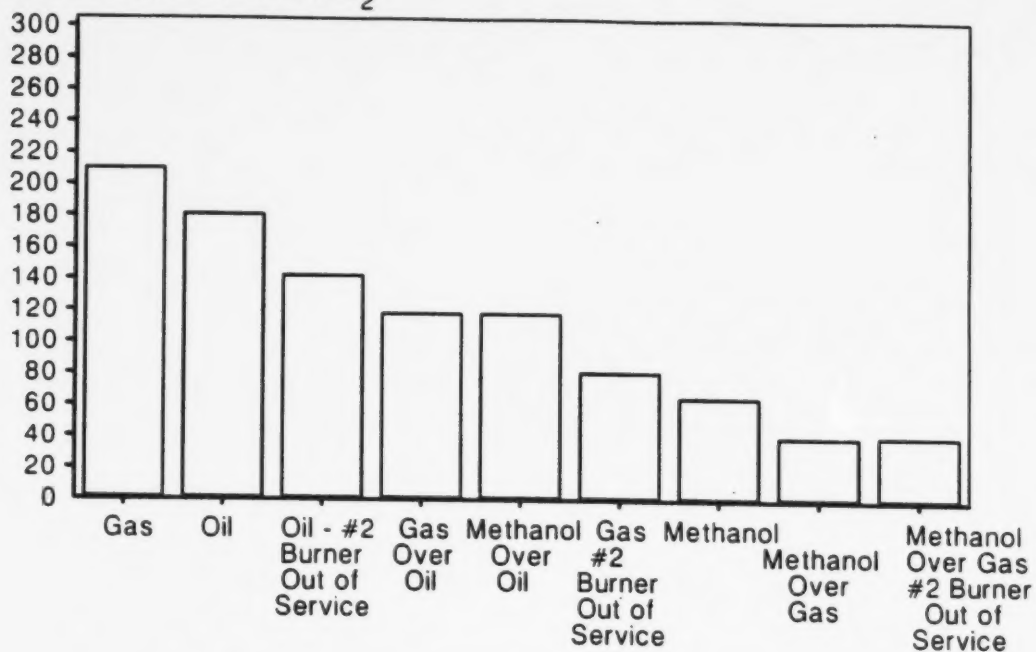


FIGURE 9: COMPARISON OF NOx EMISSIONS

APPLICATION OF FUEL BIASING FOR NO_x EMISSION
REDUCTIONS IN GAS-FIRED UTILITY BOILERS

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ABSTRACT

The effectiveness of fuel biasing in reducing NO_x emissions from gas-fired utility boilers has been evaluated by the San Diego Gas & Electric Company (SDG&E). The unit chosen for this evaluation, South Bay Unit 1, is a 150 MW face-fired unit which currently meets local NO_x emissions limits by operating with burners-out-of-service (BOOS). This operating mode results in CO emissions of greater than 2000 ppm and an O₂ imbalance.

Fuel biasing offers a reduction in NO_x emissions by controlling combustion stoichiometry in two discrete combustion stages. The first stage is operated fuel-rich in order to limit the formation of thermal NO_x, while the second stage may be operated either fuel-rich or fuel-lean. The primary advantage of fuel biasing is that it provides better control of combustion stoichiometry, which serves to reduce O₂ imbalances and increased CO emissions which may accompany BOOS operation.

The effect of fuel bias ratio, air register position, and excess oxygen level on unit emissions and performance were evaluated. The use of fuel biasing allowed the unit to meet local NO_x regulations, while decreasing the O₂ imbalance and reducing CO emissions to less than 500 ppm. Additionally, improvements in unit operating efficiency were measured when using the fuel biasing firing mode.

INTRODUCTION

The San Diego Gas and Electric Company (SDG&E) is continually evaluating means to improve the thermal efficiency of its gas- and oil-fired steam generating units while maintaining compliance with local NO_x emissions regulations. In the early 1970's, SDG&E and other major California utilities pioneered, with the support of KVB, the implementation of NO_x control techniques based on modification of the combustion process. This work led to the implementation of staged combustion through the use of burners-out-of-service (BOOS) operation to achieve NO_x emissions compliance. Many boilers within the SDG&E system, including South Bay Unit 1, currently utilize BOOS operation to maintain NO_x emissions compliance.

The use of this mode of operation on South Bay Unit 1 has, however, led to an O_2 imbalance and CO emissions of greater than 2,000 ppm. These operating conditions, which are due to the furnace configuration and burner arrangement of this unit, result in some negative impact on boiler thermal efficiency. The incremental fuel cost penalty associated with the use of these techniques is significant over the long term. Therefore, a need existed to identify alternate operating modes, on gas fuel, that could achieve compliance with the regulations without having an adverse impact on boiler performance.

This program was initiated to explore techniques for reducing NO_x emissions from SDG&E boilers while minimizing boiler thermal efficiency penalties. The technique selected for evaluation consisted of an advanced combustion process in which the fuel is biased between burner elevations. In this combustion process, the boiler is fired with all-burners-in-service (ABIS) to achieve NO_x emissions compliance, while providing uniform heat absorption within the furnace and improved combustion air distribution. The impetus for this project was previous work performed by KVB for another California utility (1, 2).

In implementing fuel biasing, the furnace is divided into upper and lower combustion zones. The lower combustion zone is fired fuel-rich to control NO_x formation. The upper combustion zone is operated fuel-lean to complete the burnout of the fuel. The stoichiometry of the two combustion zones is established by biasing the gas fuel supply from the upper to the lower burner elevation. The amount of fuel supplied to the upper burner elevation varied from 30 to 40 percent, when operating in the fuel bias mode, depending on unit load. The air registers are generally maintained wide open for all burners.

The evaluation of the fuel bias process was conducted on SDG&E South Bay Unit 1 during the period of March 1986 through May 1986. Under the direction of SDG&E, KVB, Inc. and Applied Utility Systems, Inc. (AUS) were responsible for performance of the tests and the analysis of the test data.

PROGRAM DESCRIPTION

The primary objective of the South Bay Unit 1 fuel bias evaluation program was to show that NO_x emissions can be maintained to within the San Diego Air Pollution Control District (SDAPCD) regulatory limit of 125 ppm, dry at 3% O_2 , without creating CO emissions in excess of 2000 ppm or O_2 imbalances. A secondary objective was to determine if the control of NO_x emissions, using the fuel biasing process, is accompanied by improvements in unit operational flexibility and thermal efficiency over the entire load range.

The specific program objectives consisted of the following:

- . Characterize the baseline NO_x , O_2 , and CO emissions using present combustion modification techniques and determine the effect of excess O_2 on those emissions.
- . Evaluate the effect of ABIS operation on boiler thermal efficiency and unit heat rate.
- . Evaluate the ability of the fuel bias process to control NO_x emissions to within the SDAPCD limits and determine the effect of this process on boiler thermal efficiency.
- . Identify the effect of excess O_2 and air register settings on NO_x and CO emissions while utilizing the fuel bias process.
- . Optimize the fuel bias process on South Bay Unit 1.

The fuel bias evaluation program was comprised primarily of a field testing activity with a limited amount of analysis performed to quantify the significance of the data obtained.

The testing began with a series of baseline tests to identify the emissions characteristics of the unit under present operating conditions with the No. 3 BOOS. The effects of load, excess O_2 , and firing pattern (BOOS/ABIS) on NO_x and CO emissions were quantified. The amount of attemperation used, especially at full load, was also determined. The purpose of these tests was to document the NO_x emission characteristics of the boiler under conditions typical of day-to-day operation.

Baseline data were obtained at loads of 150, 125, 100, 75, and 50 MW. A minimum of two excess O_2 levels were evaluated at each load in order to characterize the effect of excess O_2 levels on emissions and boiler operation. Complete operating data were recorded for each test condition to provide sufficient information for calculating the unit efficiency.

Following the completion of the baseline testing, fuel bias testing was performed in which gas fuel was biased vertically from the top burner elevation to the bottom burners. This method of biasing was named Uniform Fuel Biasing (UFB). In these tests, the existing gas burner shut-off valves were used to bias the fuel. Pressure gauges, installed on each burner, were used to give an indication of the biasing ratio.

The UFB tests were performed at the same loads used for the baseline tests. These tests were initiated by placing ABIS with equal gas fuel flow to both burner elevations. The fuel was then biased until the fuel pressure, at the top elevation, was near the allowable minimum for flame stability or NO_x emissions were sufficiently low to achieve compliance with the emission limits.

Following the completion of the UFB tests, additional tests performed included the evaluation of Selective Fuel Biasing (SFB) and the performance of air register adjustments. In the SFB firing mode, the gas fuel flow was biased from the center burners, on the top elevation, to the side burners on the same elevation. This resulted in operating the top center burners very fuel-lean, the upper side burners slightly fuel-lean, and the bottom burners fuel-rich. A more detailed description of the various fuel biasing modes evaluated during this project is presented below.

HARDWARE DESCRIPTION

South Bay Unit 1 is a Babcock and Wilcox front-wall-fired boiler. The unit is natural gas- and oil-fired and has a maximum generator output of 153 megawatts. The boiler operates with a forced draft furnace and is equipped with two vertical-shaft Ljungstrom regenerative-type air preheaters. The boiler provides 980,000 lb/hr steam to the turbine. Design steam conditions are 1005 °F for both superheat and reheat outlet temperatures with main steam pressure of 2150 psig. Steam temperature control is provided by spray-type attemperators and flue gas recirculation through the furnace hopper.

The test boiler has eight Peabody H-36 gas/oil burners arranged in two elevations with four burners each. The burners have 36-inch diameter throats and dual air registers, which allow control of both the swirl and amounts of air entering the inner and outer core of the flame. The location of the burners and the furnace inside dimensions are shown in Figure 1.

The test boiler is normally operated with the No. 3 BOOS when firing natural gas. Under current plant operating conditions, the air register settings are fixed for all eight burners, at loads less than maximum. One adjustment is made to the air register settings at maximum load. During the course of this test program, the boiler was operated in a number of off-design conditions. Operating changes evaluated included operation with ABIS, varying degrees of fuel biasing, and variable air register settings.

Continuous gaseous emissions monitoring was provided by SDG&E's mobile test van, which is equipped with instruments to measure the NO_x , O_2 , and CO concentrations in the combustion gases. These species were measured using (1) a TECO Model 10 chemiluminescent analyzer for NO_x ; (2) a Teledyne Model 324 fuel cell oxygen analyzer; and (3) an Anarad NDIR analyzer for CO. The instruments were calibrated periodically to ensure the accuracy of the data.

Combustion gas samples were withdrawn immediately downstream of the economizer. The sample matrix consisted of eight stainless steel probes located in the boiler economizer outlet duct. Each probe was fitted with an individual sample line for obtaining duct traverse data.

TECHNICAL DISCUSSION

The fuel bias process represents an alternate combustion modification technique for controlling NO_x emissions from gas- and oil-fired utility boilers. The technique generally provides a reduction in emissions while offering an improvement in boiler operational flexibility. In the fuel bias process, the boiler furnace is divided into two discrete combustion stages. The first combustion stage (lower furnace section) is operated fuel-rich to control NO_x formation, and the second combustion stage (upper furnace section) is operated fuel-lean to achieve the complete burn-out of the fuel. Presented in this section is a brief description of the process and its advantages over conventional combustion modification techniques using BOOS operation. The process chemistry is described in detail in Reference 1.

The fuel bias process is implemented by restoring the boiler operation to ABIS. To establish the two combustion stages, fuel flow is biased from the upper to the lower burner elevations. The degree of biasing depends upon the level of

NO_x reduction desired. As the amount of fuel biased to the lower burners is increased, a greater degree of NO_x emissions reduction is achieved. Generally, the air registers are maintained fully open to simplify the implementation of the process throughout the boiler load range.

A schematic of the fuel bias process, as implemented at South Bay Unit #1, is shown in Figure 2. In this application, the portion of the furnace volume, generally referred to as the flame basket, was divided into two approximately equal consecutive combustion zones. The first combustion zone was operated fuel-rich while the second combustion zone was operated fuel-lean. The stoichiometry of the two combustion zones was accurately controlled by varying the gas fuel flow to each burner elevation.

Fuel biasing offers an attractive option for controlling NO_x emissions from utility boilers for several reasons. The process creates two discrete combustion zones where the stoichiometry, in each zone, is essentially uniform. This inhibits NO_x formation in the fuel-rich zone and, in the absence of excess oxygen, allows for the destruction of NO_x by its reaction with certain combustion intermediates. In this case, the NO_x acts as an oxidizing agent, donating oxygen to oxidize these combustion intermediates. Combustion intermediates identified to react with NO_x in this environment, include CH₄, CO, and H₂. As a result of donating an oxygen atom, the NO is reduced to N₂.

The creation of a uniformly fuel-rich combustion environment in the first combustion stage therefore offers two advantages. The first advantage is the control of NO_x formation. The second advantage is the destruction of NO_x already formed by reaction with combustion intermediates. The combined effect of these two mechanisms offers the maximum reduction in NO_x emission levels.

Providing a fuel-lean zone in the upper furnace section allows for the complete burnout of the fuel at low excess O₂ levels with minimal CO emissions. In this case, the fuel-lean combustion provides a preheated source of oxygen to achieve the complete oxidation of the unburned fuel from the first combustion zone. The preheating of this oxygen source, by operating this combustion stage fuel-lean, enhances the penetration and mixing of this additional oxygen and promotes the complete burnout of fuel at minimum excess O₂. The uniform combustion stoichiometry established in the second combustion zone essentially eliminates O₂ imbalances experienced with BOOS operation.

The stratification of the combustion stoichiometry in the fuel bias process leads to the release of an increased amount of energy in the lower portion of the boiler furnace. This enhances heat absorption in the radiant section of the boiler and thus reduces combustion gas furnace exit temperature. The lower gas temperature, in turn, reduces the need for attemperation and leads to an improvement in plant thermal efficiency. While the intense release of energy, in the lower furnace section, would normally lead to increased NO_x emissions, maintaining the combustion fuel-rich in this zone minimizes the formation of NO_x.

A reduction in the attemperation rate is offered in the fuel bias process by maintaining an oxidizing region in the second combustion zone. This region, as discussed above, provides for the rapid oxidation of unburned fuel thus preventing delayed combustion in the convective section. The second combustion zone therefore acts as an afterburner to achieve low NO_x and CO emissions while maintaining low excess O₂ operation.

The fuel bias process offers several advantages over conventional combustion modification techniques. In conventional techniques, staged combustion is

achieved by operation with BOOS or with the use of overfire air (OFA). In both methods, air is admitted to complete the fuel burnout at low preheat levels (600°F) and low supply pressure (windbox pressure). This results in inefficient mixing of this air with the combustion products causing high CO emissions or high excess O₂ operation. If the boiler is operated at high excess O₂ to maintain reasonable CO emissions levels, the degree of combustion staging is reduced. This leads to an increase in NO_x emissions. Operation at high excess O₂ also results in reduced boiler thermal efficiency. Therefore, competing effects exist, with the use of conventional combustion modification techniques, between achieving low NO_x emissions and high boiler thermal efficiency.

BOOS operation results in severe combustion stoichiometry stratification within the furnace. Fuel-rich and fuel-lean regions are created to reflect the firing pattern. This results in having air in direct contact with the fuel-rich regions, thereby reducing the residence time available for the NO_x reduction chemistry to proceed. This compromises the effectiveness of combustion staging. BOOS operation also causes delayed combustion of the fuel, which may result in extending flames into the boiler convective section. These operating conditions can cause increased attemperation in the superheater and reheater sections and result in an efficiency penalty.

In summary, it has been shown that the fuel bias process addresses many of the limitations of conventional combustion modification techniques. The process offers an efficient burnout zone by operating the upper burners fuel-lean. Delayed burning in the convective section is reduced by providing rapid burnout in a uniformly oxidizing combustion zone. Additionally, the fuel biasing shifts the heat release to the lower furnace section, thereby enhancing heat absorption in the radiant section and minimizing the need for attemperation in the convective section.

RESULTS AND DISCUSSION

The test program encompassed tests with ABIS, BOOS, and testing of the fuel bias process. A total of five firing conditions were evaluated. Test variables included boiler load, furnace excess O₂, target CO emission level, register adjustment, and, in the case of the fuel bias process, the degree and method of fuel biasing. The effect of fuel biasing on excess O₂, NO_x and CO air emissions, and unit heat rate, as identified during the test program, is presented below.

To provide improved insight into the significance of the test results, gaseous species concentration profiles, at the boiler economizer outlet, were used to reflect the performance of individual burners. By positioning a matrix of probes at the appropriate location in the boiler economizer outlet, it was possible to make a determination as to a specific burners performance with regard to NO_x and CO emissions as well as the operating excess O₂ level. This information offered the basis for explaining boiler performance, under different firing conditions, based on the performance of individual burners. In presenting the test results, the gaseous species profiles were used primarily to compare the performance of the firing modes evaluated.

Throughout the program, trade-offs were made between controlling CO and NO_x emissions and maintaining low excess O₂ operation. The dominant requirement was compliance with the NO_x regulations. In all cases, except for ABIS testing, furnace excess O₂ was reduced to maintain NO_x emission compliance even if this reduction in O₂ resulted in increased CO emissions. In cases where NO_x emissions

compliance was readily achieved, excess O_2 was increased incrementally to reduce CO emissions to below a set maximum.

During the early stages of testing, this maximum desired CO emission level was selected at 500 ppm. However, this selection represented a stringent requirement and dictated the need to operate the boiler at increased excess O_2 levels. Motivated by the desire to improve unit thermal efficiency, the maximum CO emissions level was relaxed to 1,000 ppm to allow operation at lower excess O_2 levels. The effect of the ICNF process on unit heat rate was determined by monitoring key operating variables and calculating the heat rate based on measured values for these variables.

In implementing the fuel bias process, fuel flow was biased from the top to the bottom burner elevation. As discussed previously, two methods of fuel biasing were implemented: uniform fuel biasing (UFB) and selective fuel biasing (SFB). In SFB, fuel was supplied to the upper elevation burners at varying amounts. In this case, the two side burners on the top elevation were biased to a higher degree than the two center burners on the same elevation. Several SFB patterns were evaluated to identify firing conditions producing the most favorable performance.

EFFECT OF THE FUEL BIAS PROCESS ON EMISSIONS

To evaluate the NO_x reduction capability of the fuel bias process, initial testing was performed to obtain baseline NO_x emission data while operating both with the No. 3 BOOS and ABIS. Following this, fuel bias ratios were varied to characterize the fuel bias process performance. UFB was evaluated at all loads, while SFB was evaluated at loads of 100 MW and greater. The results of these tests are presented in Figure 3, where NO_x emissions are plotted versus fuel bias ratio as a function of load. The data show that SFB was most effective at loads of 100 MW and above. At fuel bias ratios of about 35/65, NO_x reductions of nominally 30 percent were measured. The reductions were found to be independent of load or initial NO_x levels. Implementation of SFB, in which the fuel in the upper burner elevation was biased 60 percent to the outer burners (Nos. 1 and 4) and 40 percent to the inner burners (Nos. 2 and 3) provided additional NO_x reductions of nominally 10 percent.

For each load evaluated, optimum fuel bias conditions were chosen based on NO_x and CO emissions as well as excess O_2 levels. These data are presented in Figure 4, where NO_x emissions, for the five combustion modes evaluated during the program, are compared as a function of boiler load. Of significance is that the boiler is capable of complying with NO_x emission limits when operating with ABIS at loads up to 125 MW. Since low CO and excess O_2 operation are readily achieved when operating with ABIS, the data suggest that boiler operating procedures should be modified to operate with ABIS up to 125 MW load. In addition to reducing CO and NO_x emissions, operation with ABIS is expected to provide efficiency benefits in terms of reduced attemperation rate and lower stack losses.

Operation with ABIS resulted in the highest NO_x emission levels for all boiler loads. This result is expected since, in this operating mode, the combustion process is not modified to control NO_x formation. NO_x emission levels produced by the other firing modes were for the most part comparable. The lowest NO_x emission level was invariably achieved with SFB, indicating that this firing mode offers the most attractive NO_x control option.

NO_x concentration was measured in the boiler economizer outlet to determine individual burner contributions to total NO_x emissions. The results of these

measurements, for different boiler loads, are presented in Figure 5. In this figure, the data are again presented for three firing modes: B00S using existing plant register adjustments, fuel biasing utilizing either UFB or SFB, and ABIS. The NO_x data showed that Burner Nos. 1, 2, 5, and 6 produced lower NO_x than the remaining burners. This trend is more obvious at loads in excess of 100 MW and when operating with the No. 3 B00S. Nevertheless, this trend is repeated, regardless of the load or firing pattern, for all conditions evaluated during this project.

A bar graph comparing excess O_2 as a function of boiler load for the five firing modes evaluated is presented in Figure 6. These data show that excess O_2 varied over a broad range, depending upon the boiler load and firing conditions. As expected, excess O_2 levels of less than 1% were achieved throughout the boiler load range tested when operating with ABIS. Comparable excess O_2 levels were obtained with UFB and SFB firing modes except at loads above 125 MW. The highest excess O_2 levels were measured during modified B00S operation.

Excess O_2 data, in its absolute value, did not reflect any unique characteristics of the combustion modes tested. The actual value recorded, under any test condition, was governed by the ability of the boiler to comply with the NO_x emissions limit and the desire to maintain CO emissions at a minimum. If the boiler was unable to comply with the NO_x emission limit, excess O_2 was reduced, at the expense of increasing CO emissions, to achieve NO_x compliance. This was the case for most of the B00S testing. For this reason, low excess O_2 values should not necessarily be viewed as an indication of efficient boiler operation. In many cases, the reduction in excess O_2 was obtained at the expense of increasing CO emissions, leading to the less efficient boiler operation. The CO emissions threshold varied during the course of the program for the reasons outlined previously, resulting in a lack of consistency for comparing the excess O_2 values for different test conditions.

The data presented in Figure 7 compare the excess O_2 distribution in the boiler economizer outlet, reflecting specific burner positions. The graphs are prepared for boiler loads of 75, 100, 125, and 150 MW and for the following three firing conditions -- (1) ABIS; (2) B00S, using existing plant register adjustments; and (3) fuel biasing, using either UFB or SFB, depending on load.

While the absolute value of excess O_2 level for the different firing conditions is not of significance, the data presented in Figure 7 reveal important insight into the nature of the air and fuel distribution within the boiler. These data show that, regardless of load and firing mode, Burner Nos. 3, 4, 7, and 8 received more air (or less fuel) than the remaining burners. These burners are grouped in the west side of the boiler. The poor distribution of combustion air (or fuel) existed irrespective of register adjustment and variation in fuel supply to individual burners. The result thus suggested that major deficiencies in the boiler windbox and combustion air feed system, or the gas fuel supply system, have caused the identified poor air (or fuel) distribution. Changes in register adjustment and/or fuel flow, to individual burners, represented second order changes which had little or no effect on the combustion air distribution.

To further characterize air distribution in South Bay Unit #1, the percent deviation in excess O_2 , from the average value measured for the boiler, was determined as a function of burner location. A negative percent deviation would indicate a burner starved for air, while a positive percent deviation would indicate an air rich burner. A burner position with a zero percent deviation would

indicate that the excess O_2 , at that burner position, is equal to the boiler average. The details of this analysis are presented in Reference 3.

This calculation offered a means to normalize the effect of random excess O_2 values for different firing modes. The excess O_2 percent deviation thus provided a quantitative indication as to the change in air supply from one burner position to another as a result of changes in boiler operating variables.

The results of the excess O_2 percent deviation analysis confirmed early observations that certain burners operate at lower air (or higher fuel) supply than others regardless of boiler load, register adjustment, or fuel distribution. The percent deviations for Burner Nos. 3, 4, 7, and 8 were consistently positive, suggesting that these burners are operating air rich (or fuel lean). In contrast, the percent deviations for Burner Nos. 1, 2, 5, and 6 were consistently negative, suggesting that these burners are operating air lean (or fuel rich). The magnitude of the percent deviation did not vary significantly with the firing mode. This indicates that burner related variables (register adjustment and fuel supply) did not greatly influence the degree of air stratification.

At boiler loads of 125 MW and above, the CO emissions obtained for the different firing modes were directly dependent upon the ability of the boiler to comply with NO_x emission limits. If compliance with the NO_x limit was readily achieved, excess O_2 was generally increased to reduce or eliminate CO emissions. As a result, increased CO emissions for these loads should be viewed as an indication of the difficulty that was experienced in achieving NO_x emissions compliance. This difficulty generally led to a reduction in excess O_2 , resulting in a corresponding increase in CO emissions.

At boiler loads less than 100 MW, compliance with NO_x emission limits was readily achieved for all firing modes. In this case, CO emissions more or less reflected the firing mode's sensitivity to excess O_2 . As this sensitivity increased, so did the tendency to obtain higher CO emissions. CO emissions for different firing modes were somewhat influenced by variations in excess O_2 levels.

A comparison of CO emissions for all firing modes tested, is presented in Figure 8 as a function of boiler load. These data are presented for conditions where NO_x emissions compliance has been achieved except for the 150 MW test with ABIS. The data show that operation with BOOS (first and second bars in the chart) has made the boiler susceptible to increased CO emissions. This trend existed independent of boiler load. At a boiler load of 150 MW, where reduced excess O_2 operation was required to achieve NO_x emissions compliance, increased CO emissions resulted with BOOS operation.

The increased sensitivity of CO emissions to excess O_2 , as a function of firing mode, is believed to be a manifestation of the poor distribution of combustion air or fuel gas within the boiler. Unlike ABIS or fuel bias firing, BOOS firing results in an incremental increase of nominally 15 percent in fuel supply to active burners. This causes burners that are already starved for air, due to poor air or fuel gas distribution, to operate very fuel rich. Such operating conditions result in an increase in CO emissions at an exponential rate. In ABIS firing, the fuel appears to be equally distributed to all burner positions. Similarly, when operating in the fuel bias mode, the degree of fuel stratification is much less than in the BOOS firing mode.

To provide improved insight into variables affecting CO emissions, under the various firing modes and at different boiler loads, CO concentration was measured in the boiler economizer outlet to identify the performance of individual burners. These data are presented in Figure 9. Similar to excess O₂ data, the CO data showed that selected burners are responsible for the total CO emissions from the boiler. Irrespective of boiler load, Burner Nos. 1, 2, 5, and 6 produced excessive CO emissions. These same burners were identified previously to be starved for air (or fuel rich). The data thus show that increased CO emissions are the direct result of poor air or fuel distribution. This phenomenon is aggravated when operating with BOOS where fuel rich combustion is established by increasing fuel supply to active burners.

The data presented in Figure 9 are for three firing modes; BOOS using existing register adjustments, fuel biasing, using both UFB and SFB as load conditions require, and ABIS. As can be seen in these data, CO emissions were significantly higher with BOOS firing. It is interesting to note, however, that for burners identified to be susceptible to increased CO emissions, CO concentration in the boiler economizer outlet, were detected for all firing modes. This result strongly suggests that CO emissions are dependent on burner position and air/fuel distribution to the burner rather than the boiler firing mode.

As discussed above, Burner Nos. 1, 2, 5 and 6 have been identified to operate at the lowest excess O₂ level and result in the production of increased amounts of CO. These burners also had consistently lower NO_x emissions, which can be the result of operating these burners in the staged combustion mode. The consistency between NO_x, CO, and O₂ data have lent credibility to the assumption that gaseous species concentration measurements made at the boiler economizer outlet do indeed reflect the firing conditions of individual burners.

As a result of these findings, additional studies were performed (4) to determine the causes of the O₂ maldistribution. This work showed the O₂ maldistribution primarily to be due to a fuel imbalance resulting from non-uniform fuel orifice sizes in the gas burner rings.

IMPACT OF FUEL BIASING ON BOILER EFFICIENCY AND UNIT HEAT RATE

The impact of the fuel bias process on boiler efficiency and unit heat rate was examined to quantify if compliance with NO_x emissions, using this firing mode, would result in a penalty or an improvement in unit heat rate. The efficiency variables examined included attemperation in the superheater and reheater sections as well as overall unit heat rate.

A comparison of attemperation rates for three different firing modes is presented in Figure 10. These data showed that ABIS operation results in the lowest attemperation levels. This is expected since, in this firing mode, combustion is most efficient. The data also showed, however, that fuel biasing typically provided a significant reduction in attemperation rate over BOOS operation. This result, coupled with the fact that fuel biasing provided reductions in excess O₂ and CO emissions, indicates that fuel biasing should offer an improvement in unit heat rate and boiler thermal efficiency.

To quantify the effect of the firing mode on efficiency, analyses were performed to determine unit heat rate for the various firing modes tested. The unit heat rate was determined based on net megawatts produced and the amount of fuel supplied to the boiler. The data were then corrected to design steam

temperatures and back pressure using correction factors supplied by SDG&E. The results of these analyses are presented in Figure 11.

The data presented in Figure 11 verified that the use of fuel biasing has indeed improved unit heat rate compared to BOOS firing. As expected, the best heat rates were invariably obtained when operating with ABIS. In this firing mode, the heat rate progressively decreased as the unit load increased, reflecting the improvement in combustion efficiency achieved at higher loads. For the two other firing modes (BOOS and fuel biasing), a similar trend for heat rate was displayed until the unit reached full load. At full load, the modification of the combustion process, required to achieve compliance with NO_x emission limits, caused the combustion efficiency to deteriorate. This was accompanied by an increase in attemperation. This, in turn, was primarily responsible for the increase in heat rate that is displayed by the data.

The heat rate analysis clearly showed that fuel biasing provides an improvement in heat rate over BOOS firing. This improvement was obtained over the investigated boiler load range. The improvement identified was significant at full load, where it is more difficult to comply with NO_x emission limitations.

SUMMARY

The primary objective of the fuel biasing evaluation program was to show that NO_x emissions can be maintained to within the SDAPCD regulatory limit, on South Bay Unit No. 1, without creating conditions of increased CO emissions or boiler O_2 imbalances. A secondary objective was to identify if the control of NO_x emissions, using the fuel bias process, is accompanied by an improvement in unit operational flexibility and efficiency over the entire load range.

The test program encompassed gas fuel tests with ABIS, BOOS, and testing of the fuel bias process. A total of five firing conditions were evaluated. The test variables included boiler load, furnace excess O_2 , target CO emission level, register adjustment, and in the case of the fuel bias process, the degree and method of fuel biasing. Two firing modes using fuel biasing were evaluated, including (1) uniform fuel biasing (UFB), in which fuel from the top burner elevation was biased an equal amount for each of the top burners to the bottom burners, and (2) selective fuel biasing (SFB), in which the firing of individual burners on the top elevation was varied to achieve optimal performance.

A comparison of the performance of the five firing modes tested is presented in Figure 12. This figure presents a summary of all gaseous species measurements made, as a function of boiler load, for the different firing modes. Figure 12 represents a regrouping of data already discussed under previous subsections to allow the review of all the data in the form of a summary.

As can be seen in this figure, the excess O_2 data varied between tests for the different boiler loads and firing modes, since guidelines used for determining boiler excess O_2 were changed during the course of the program. The CO data showed that BOOS firing is conducive to increased CO emissions, especially at high boiler loads where it is more difficult to achieve NO_x emissions compliance. Of all firing modes tested, fuel biasing achieved all desired operating criteria. It allowed operation at O_2 levels comparable to those with ABIS and achieved NO_x emissions compliance at all loads with a sufficient margin. Fuel bias operation, utilizing either UFB or SFB, also resulted in minimal CO emissions. The fuel bias data thus showed that both the UFB and SFB firing modes may represent attractive NO_x control techniques that would allow South Bay Unit #1 to comply with NO_x emission regulations.

The fuel bias process also offered an improvement in unit heat rate when compared to BOOS firing. This was most noticeable at higher loads, where it is more difficult to comply with NO_x emission regulations.

CONCLUSIONS

The most important results obtained during this program are summarized below:

- Compliance with NO_x emission regulations can be achieved on South Bay Unit No. 1 by the implementation of fuel biasing. Uniform fuel biasing was selected for loads of 75 and 100 MW, while selective fuel biasing was chosen for loads of 125 and 150 MW. Using these firing modes, low NO_x emissions were attained at low excess O_2 levels with minimal CO emissions. The fuel bias firing modes have also offered satisfactory reductions in unit heat rate.
- Combustion species profiles at the boiler economizer outlet indicate severe stratification of combustion air or fuel distribution. This stratification existed irrespective of register adjustment or degree of fuel biasing and/or burner firing patterns. The stratification is believed to be caused by design deficiencies in boiler windbox and combustion air feed system or due to imbalances in the gas fuel feed system.
- BOOS operation results in CO emissions of greater than 2000 ppm. Based on gaseous species profiles, selected burners (1, 2, 5, and 6) determine the amount of CO generated. These burners are susceptible to increased CO emissions due to poor combustion air or fuel distribution. The maldistribution of combustion air or fuel also causes increased levels of NO_x emissions to be generated by burners 3, 4, 7 and 8.
- Minimum NO_x and CO emissions are obtained when the concentration of combustion species across the boiler back passages is more or less uniform.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the view of the Agency and no official endorsement should be inferred.

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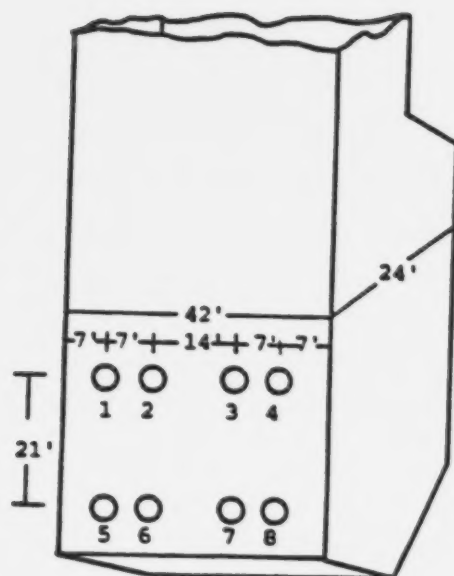


Figure 1. General burner arrangement and numbering scheme - SDG&E South Bay Unit 1.

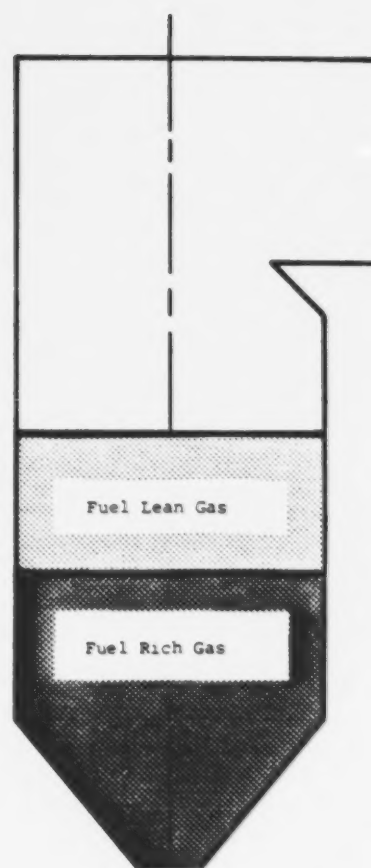


Figure 2. ICNF process schematic as implemented at South Bay Unit 1.

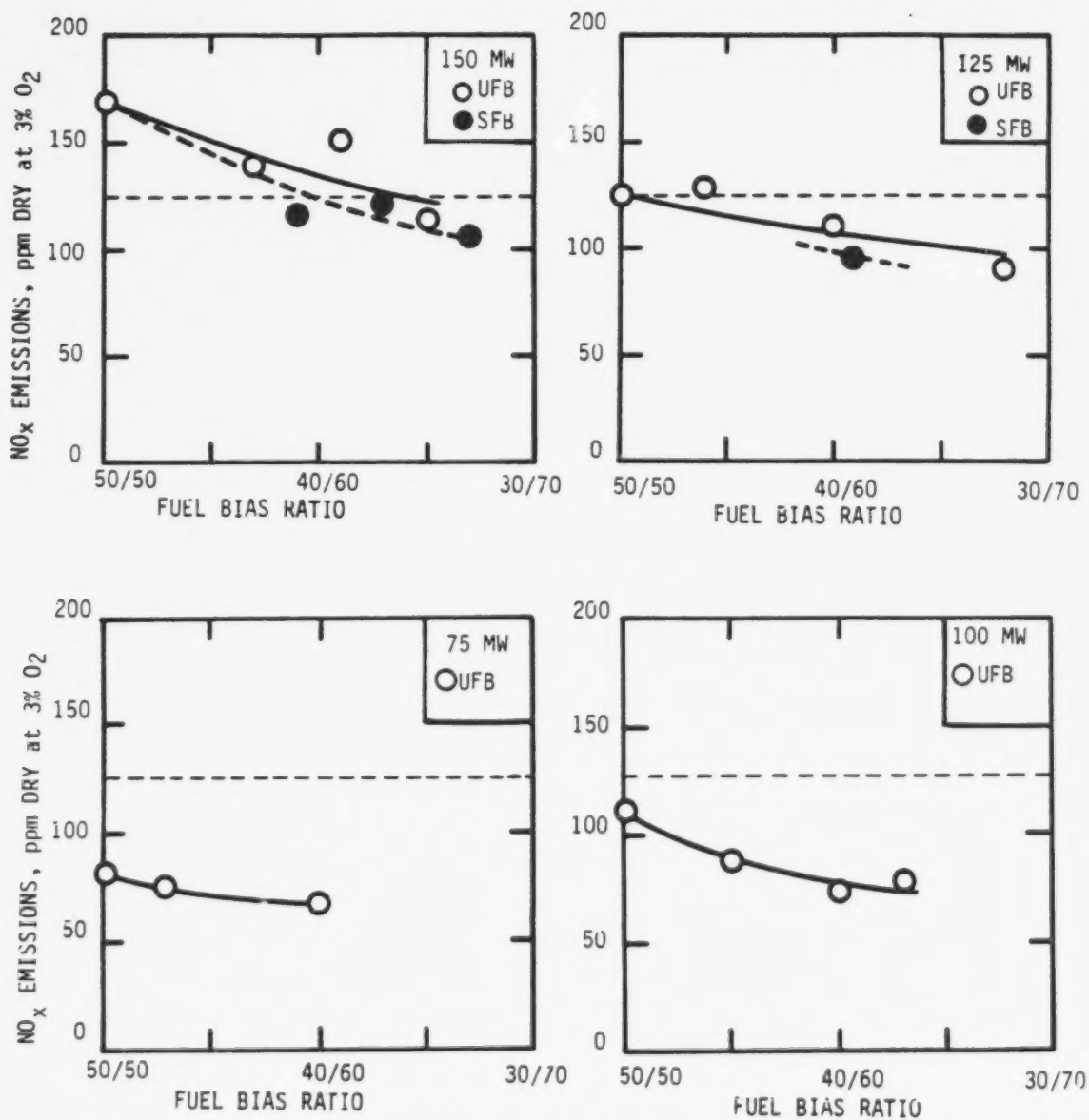


Figure 3. NO_x concentrations as a function of fuel bias ratio. Ratio on horizontal axis represents fuel ratio, on a Btu basis, between the top and bottom burner elevations. Dotted line represents SDAPCD NO_x emissions limit of 125 ppm, dry at 3% O₂.

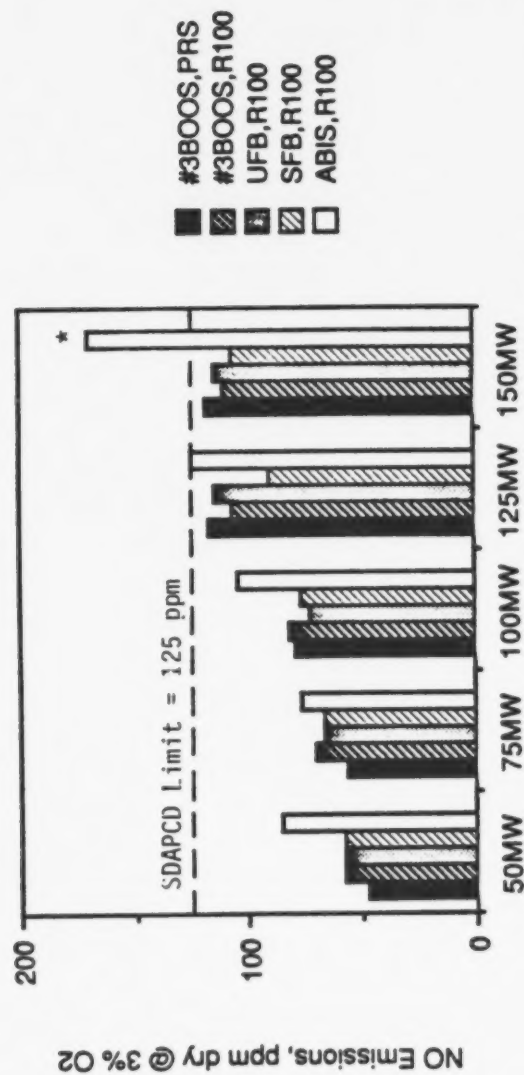


Figure 4. Variation in NO emissions as a function of boiler load. PRS indicates plant register settings, and R100 indicates all registers set at 100 percent.

*Operation under NO_x emission variance granted by SDAPCD.

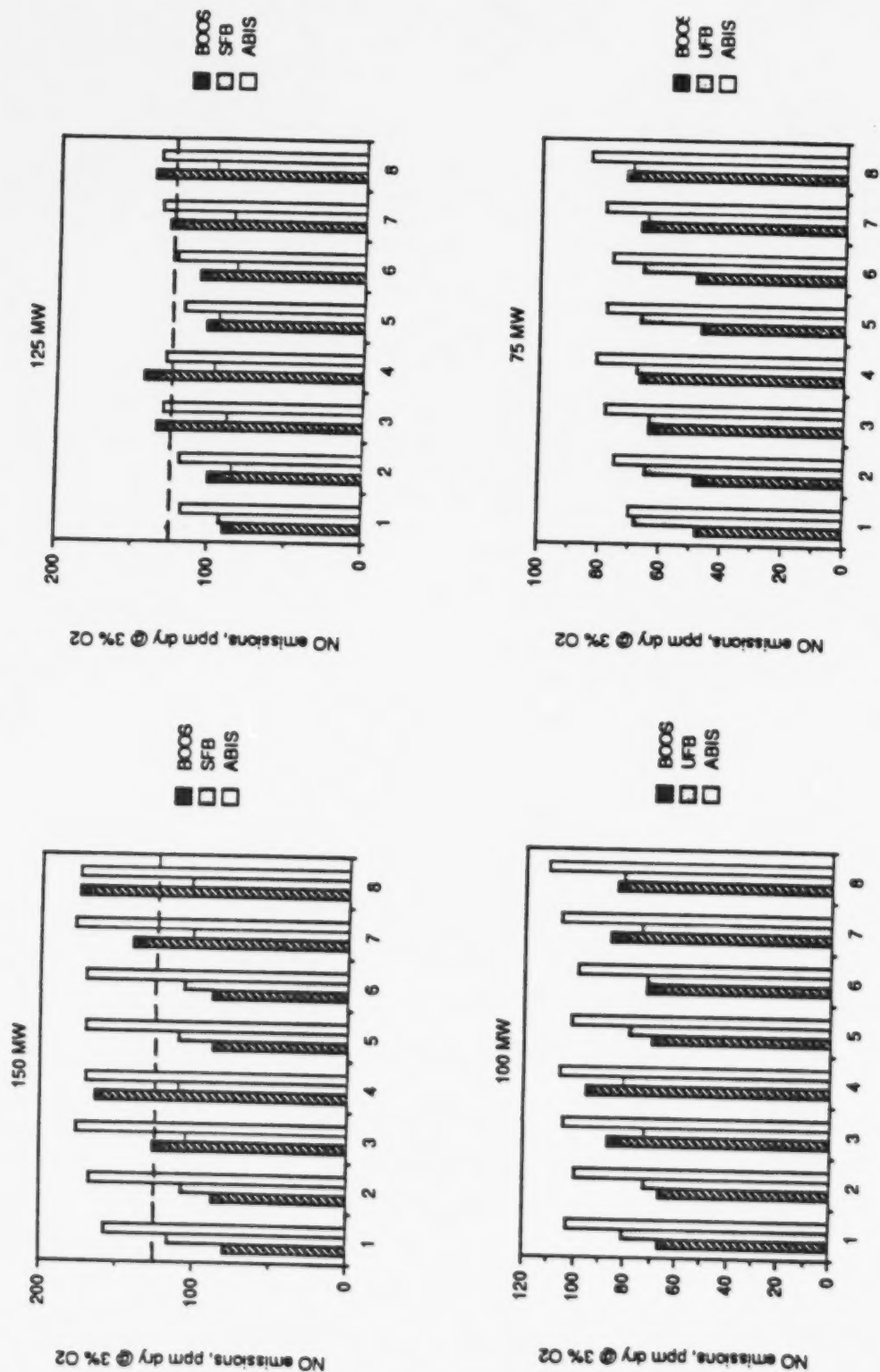


Figure 5. NO concentrations as a function of burner position. Dashed lines on plots for 125 and 150 MW indicate SDAPCD NO_x limit of 125 ppm.

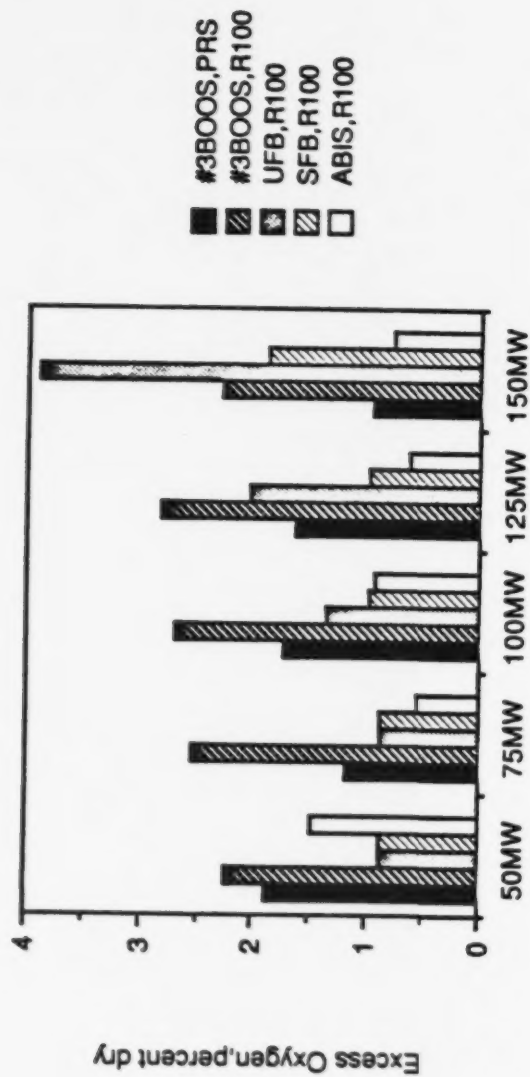


Figure 6. Variation in excess oxygen as a function of boiler load. PRS indicates plant register settings and R100 indicates all registers set at 100 percent.

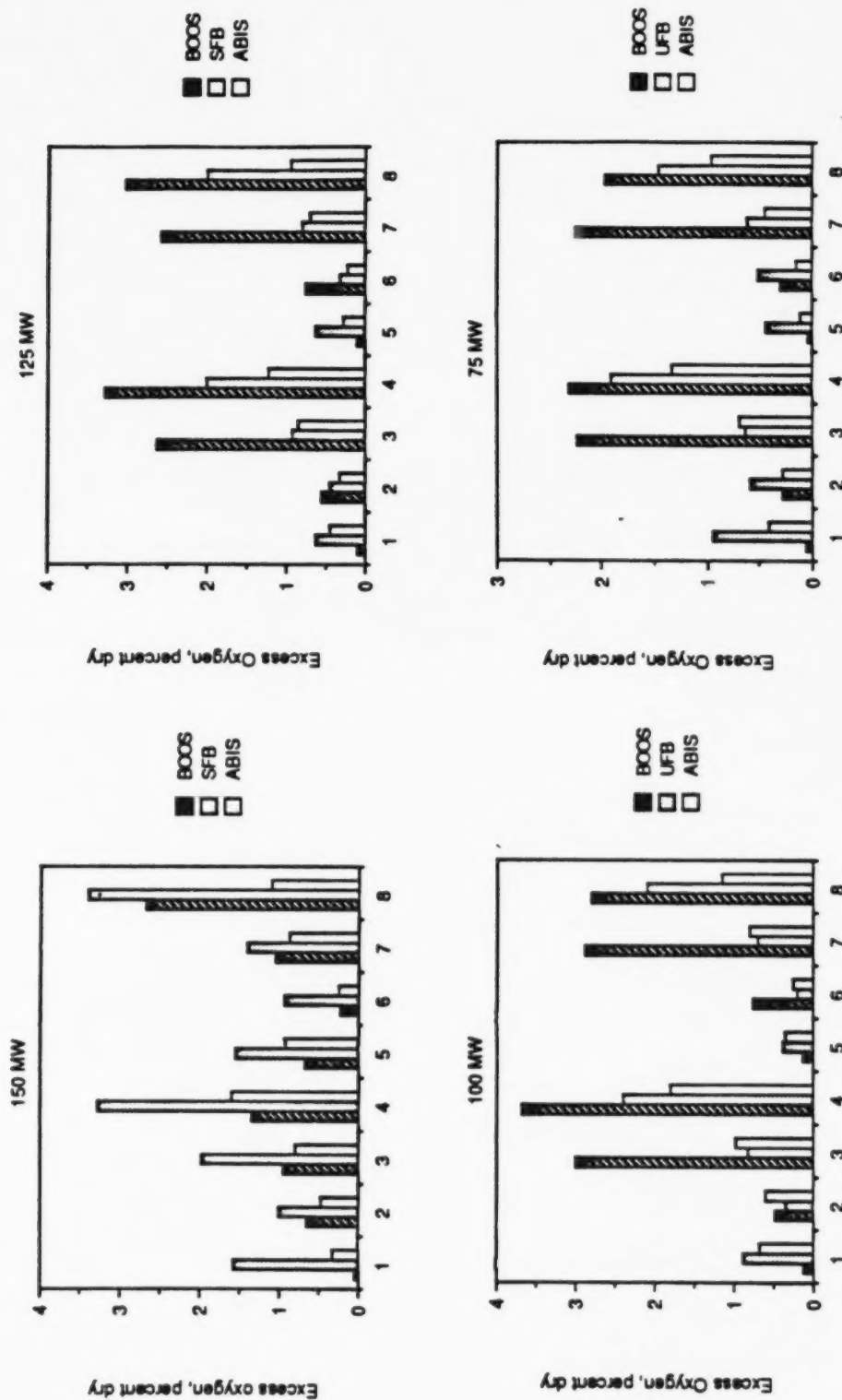


Figure 7. Excess O_2 as a function of burner position.

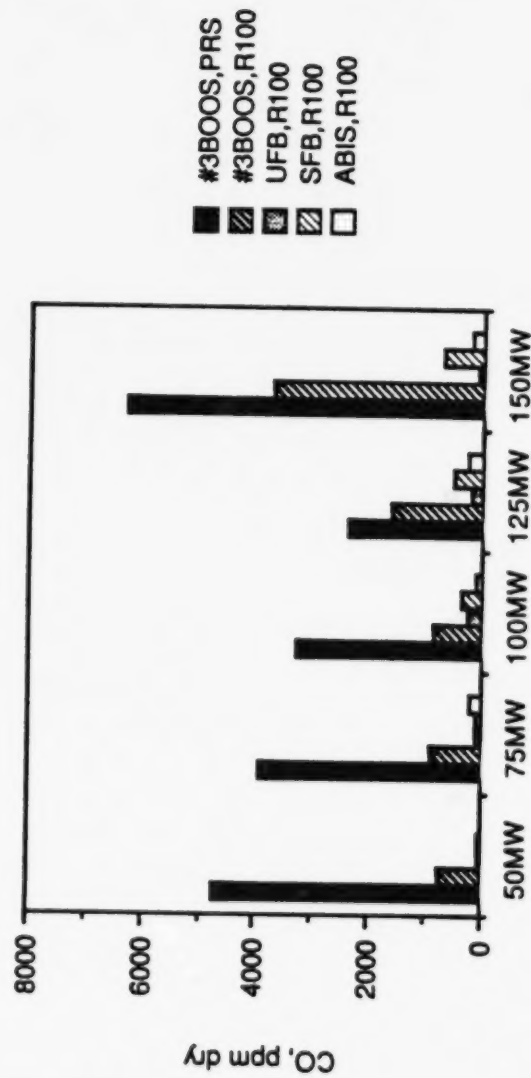


Figure 8. Variation in CO emissions as a function of boiler load. PRS indicates plant register settings, and R100 indicates all registers set at 100 percent.

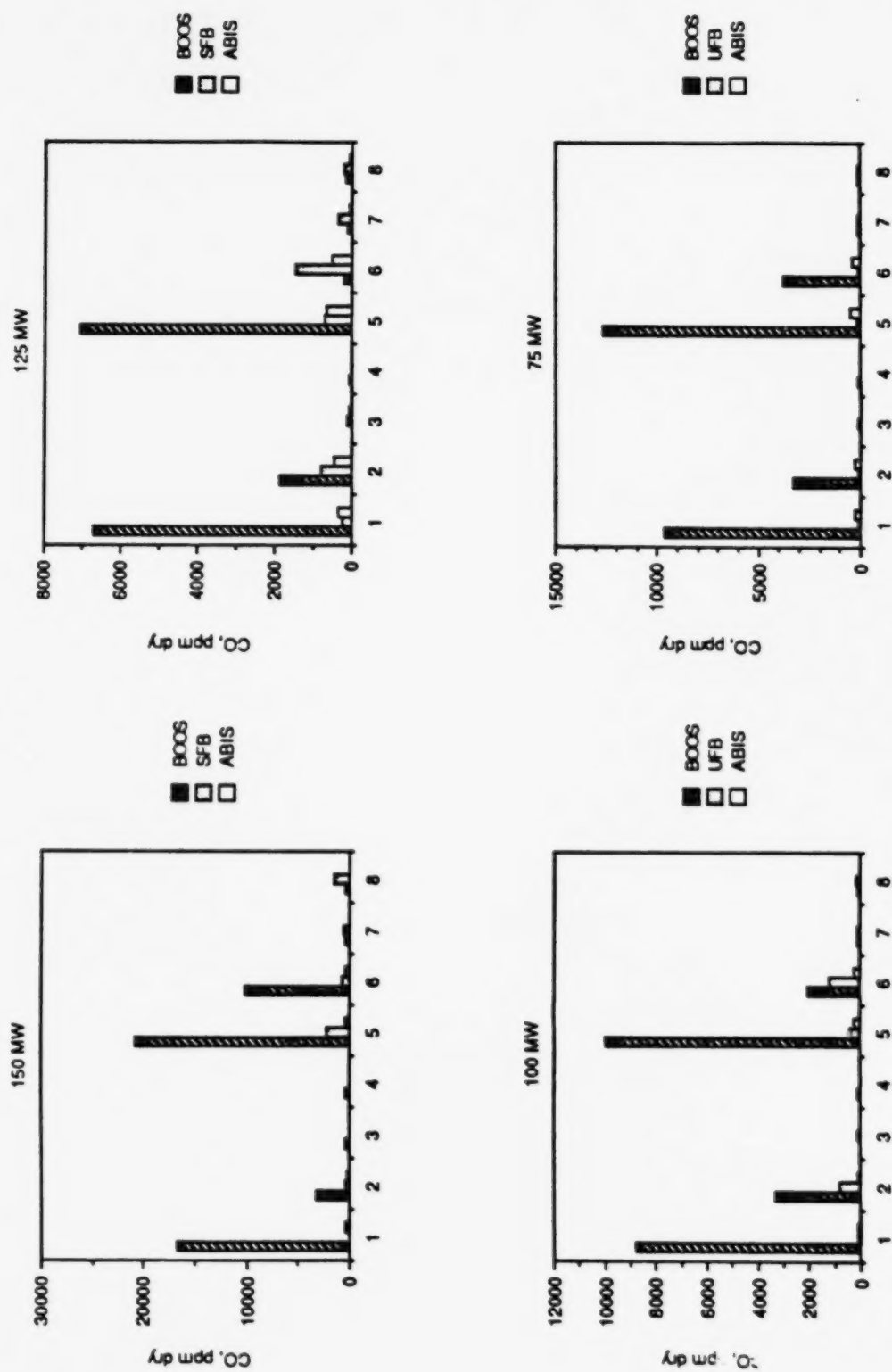


Figure 9. CO concentration as a function of burner position.

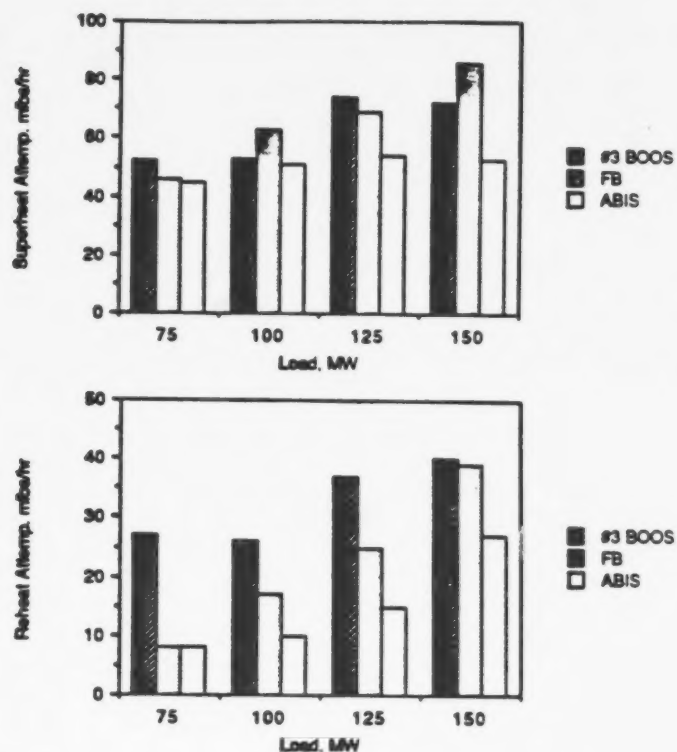


Figure 10. Effect of firing mode on superheat and reheat attemperation. When operating in FB firing mode, uniform fuel biasing used at 75 and 100 MW and selective fuel biasing used at 125 and 150 MW.

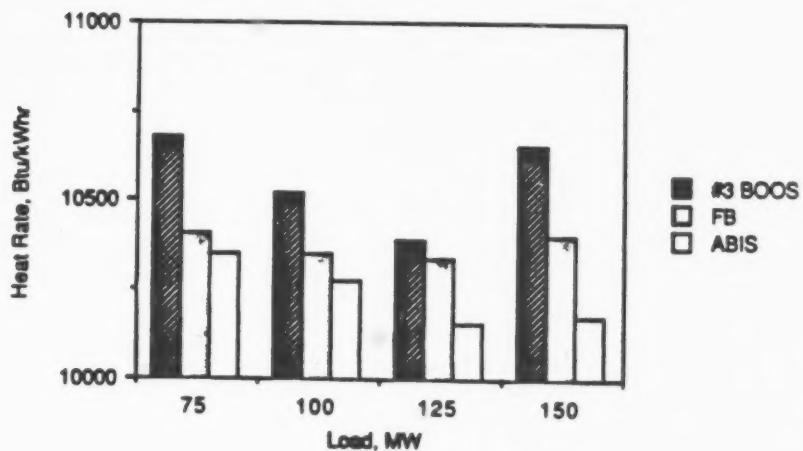


Figure 11. Effect of firing mode on unit heat rate. When operating in FB firing mode, uniform fuel biasing used at 75 and 100 MW and selective fuel biasing used at 125 and 150 MW.

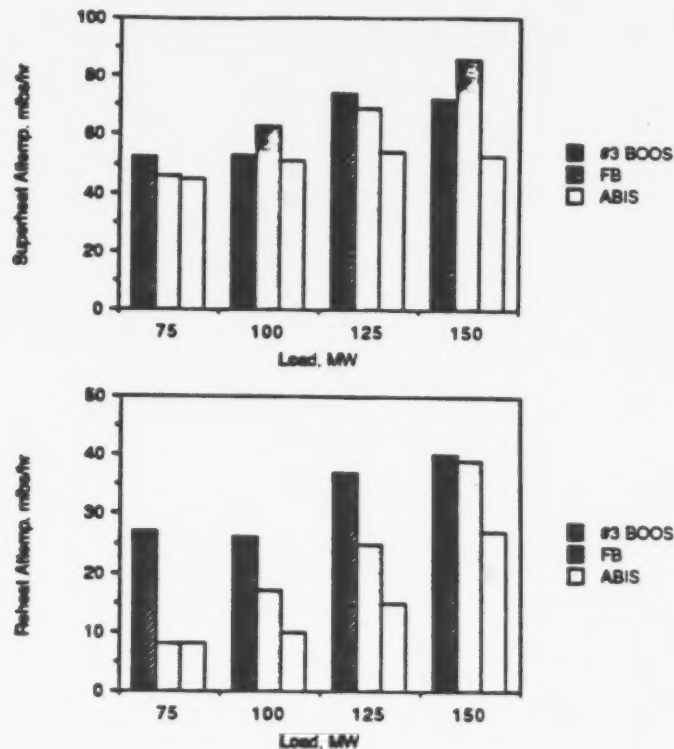


Figure 10. Effect of firing mode on superheat and reheat attemperation. When operating in FB firing mode, uniform fuel biasing used at 75 and 100 MW and selective fuel biasing used at 125 and 150 MW.

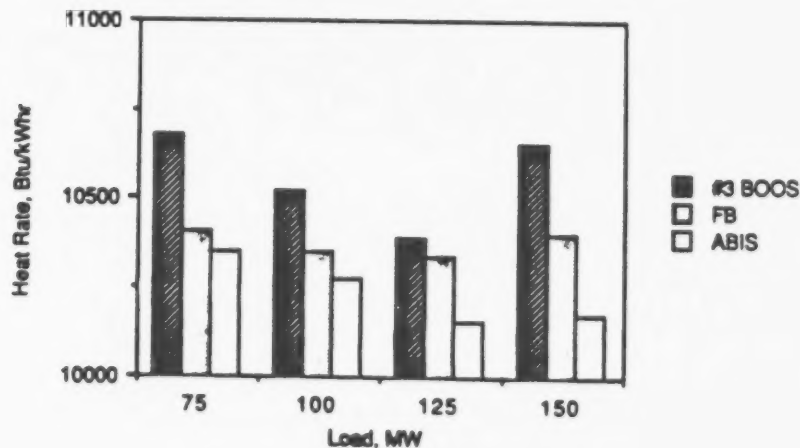


Figure 11. Effect of firing mode on unit heat rate. When operating in FB firing mode, uniform fuel biasing used at 75 and 100 MW and selective fuel biasing used at 125 and 150 MW.

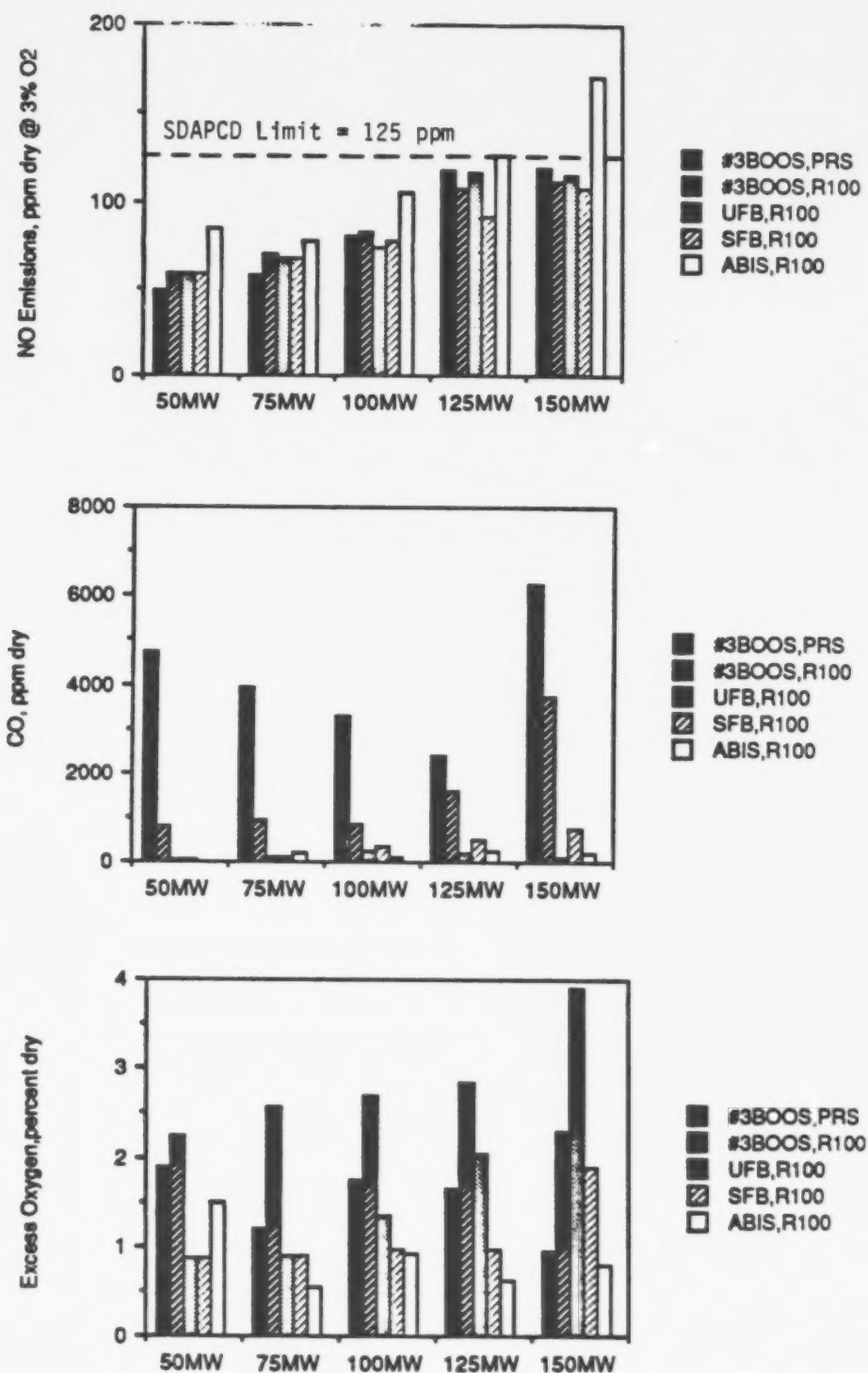


Figure 12. Summary of gaseous species measurements. PRS indicates plant register settings and R100 indicates all registers set at 100 percent.

NO_x INVENTORY AND RETROFIT ASSESSMENT

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ABSTRACT

The Empire State Electric Energy Research Corp. (ESEERCO) has funded a program to develop a model for estimating NO_x emissions from the New York Power Pool (NYPP) electric system for different generation dispatch scenarios. Base-line emission levels for each boiler and for the entire system were calculated. In addition the technical feasibility, NO_x reduction potential, and costs of commercially available NO_x control technologies were evaluated for each boiler. Besides quantifying annual NO_x emission rates for NYPP fossil fuel fired power plants, the model enables ESEERCO to evaluate the effectiveness and costs of alternative NO_x reduction strategies.

INTRODUCTION

Recently, federal and state regulatory authorities have focused considerable attention on existing utility boilers which in most cases, have been free of NO_x control requirements. This new interest is motivated by several factors: (1) the retirement of older units is proceeding at a rate much lower than originally forecast; (2) new utility boilers are exclusively coal units which are higher NO_x emitters; and (3) NO_x is believed to play a significant role in the acidification of rainfall in the northeastern United States.

In anticipation of possible changes in NO_x emission regulations (the scope of which make them no longer a single utility issue), the Empire State Electric Energy Research Corporation (ESEERCO) contracted with KVB, Inc. and Electric

Power Technologies, Inc. (EPT) to perform a study to assess the NO_x emissions from fossil fuel power plants in the New York Power Pool (NYPP), which includes all the power generating companies in New York State.

The objective of the program was to develop a model for estimating baseline NO_x emissions from the NYPP electric system for different generation dispatch scenarios. In addition, the technical feasibility and corresponding costs for reducing NO_x were to be addressed. Accordingly, the study evaluated commercially available control technologies and their applicability to individual plants. The model and related technical information enables ESSERCO to quantify annual NO_x emission rates and to evaluate the effectiveness and costs of alternative NO_x reduction strategies. The strategies considered were as follows:

1. Minimum Capital Investment per ton-year of NO_x removal
2. Minimum levelized annual cost per ton of NO_x removal
3. Maximum NO_x removal without the use of post-combustion treatment
4. Maximum NO_x removal with post-combustion treatment, where applicable
5. Ease of implementation in terms of outage requirements, risk, and impact on day-to-day operations

ESSERCO PROGRAM DESCRIPTION

A schematic outlining the program elements is presented in Figure 1 for both the baseline and controlled NO_x emissions determination.

DATA ACQUISITION

Referring to the Figure, the first task of the program comprised the data acquisition activity. The initial process began with the development of a questionnaire form listing the required information. The forms were sent to all utilities within the NYPP requesting detailed and comprehensive information grouped within the following general categories: (1) Boiler Data, (2) Burner Data, (3) Fuel Analysis, (4) Fuel Use Patterns, (5) Emissions Data, and (6) Operating Data. The data obtained from the questionnaires was reviewed, and formed the basis for more specific questions regarding each of the 98 active boilers in the system. The second phase of this activity was to visit the stations to resolve questions on the submitted information, acquire and discuss more detailed information pertinent to any testing which had been performed, boiler design, operational, and fuel characteristics, and physically inspect each boiler. These visits were extremely valuable in identifying normal boiler operation, unique design features, and operational or equipment limitations.

INFORMATION PROCESSING AND REVIEW

Once accumulated, all of the acquired data was organized and tabulated in a format suitable for computer input. Boiler physical characteristics and fuel properties were used to allow characterization of the boiler population in terms of design features which affect emissions, the retrofit potential of various control technologies, and existing NO_x levels. Boiler design categories were developed into which the existing population could be sorted. Establishing these categories provided a format for assembling the data base and allowed the data base to be manipulated to characterize NO_x emissions (controlled and uncontrolled) for various design categories. Once compiled, all the information was again reviewed. Information which was inconsistent, missing, or of questionable accuracy was highlighted and these problems resolved.

EMISSION FACTOR DEVELOPMENT

The program was based on the utilization of actual NO_x emission data and, for cases where no data exist, upon predicted values. No field testing for the purpose of measuring NO_x emissions was conducted in the program. Review of the data base indicated that for approximately 43% of the population, measured NO_x test data was available. If the data was found to be consistent and pertinent to current operation it was used.

The prediction of NO_x emission factors over the unit load range for those units with no measured data was based on correlations developed from the extensive KVB and EPT data base. The primary correlating parameter for coal-fired units was unit design type and size, while for the oil and gas fired units, burner zone heat release (furnace heat release/burner zone cooling area) was used. Heat release, in millions of BTU/Hr, was determined from heat rate and load, or fuel flow and fuel higher heating value (or both as a check). The burning zone cooling area is the surface defined by the furnace width, furnace depth, and the height of the burner zone (vertical distance between the top and bottom row of burners plus half a burner elevation above the top row and below the bottom row). Data from a unit with measured NO_x data and the same burner zone cooling area would be used to estimate the NO_x emissions for the unit for which no data was available. Corrections were made to account for differences in operating excess air levels and for oil fuels, for differences in fuel nitrogen. Fuel nitrogen corrections were made using the following correlation¹:

$$NO_x^{fn} = \%N / 0.1(21.5 + 0.55(TA - 80) - 9.5(\%N - 0.28))$$

where NO_x^{fn} = NO_x attributable to conversion of fuel nitrogen
%N = fuel nitrogen content, % by weight
TA = burner theoretical air, %

The measured data reported was compared to the EPA AP-42 emission factors, and generally found to be lower. Specifically, for the following unit classes, the comparison of measured vs AP-42 predicted full load values were as follows:

- ° Tangentially fired, oil fuel: AP-42 provides a reasonable approximation of the average of the measured data, however there is considerable variation within the measured data of approximately a factor of 2 for this class of unit.
- ° Tangentially fired, gas fuel: AP-42 predictions are a factor of 2 higher than measured values.
- ° Tangentially fired, coal: AP-42 predictions compare well with the average of the measured data, however there was a 50% measured data scatter among units of this type.
- ° Wall fired, gas/oil/coal: AP-42 overpredicts the oil-fired units by 65%, the gas-fired units by a factor of 2, and the coal-fired units by 20%.

BASELINE EMISSIONS

For each unit and fuel, polynomial curve fits of NO_x emissions and Heat Rate over the load range were generated. Hourly NO_x emissions (lb/hr) for each unit were calculated assuming constant operation for each hour according to the following formula:

$$\text{NO}_x(\text{lb/hr}) = \frac{\text{ppm NO}_x \times \text{Heat Rate} \times \text{MW}}{K_{\text{fuel}}}$$

where ppm NO_x = polynomial function of MW
 Heat Rate = polynomial function of MW
 MW = unit load for hour
 K_{fuel} = fuel conversion factor, ppm/(lb/10⁶BTU)

These hourly rates were then summed for a daily rate using actual load history data for eight typical seasonal days (4 seasons, one typical week day, one typical weekend day). A monthly rate was calculated by weighting week days by 5 and weekend days by 2 for the appropriate days per month. The values for each month were then summed to obtain annual NO_x emissions in tons/year.

The distribution of installed capacity in the NYPP by design type and fuel is shown in Figure 2. As can be seen, over 80% of the generating capacity is provided by oil and gas fired units, with tangentially-fired units by far the largest single design type.

Baseline NO_x emissions were estimated for the NYPP system with 1984 as the base year. The results are shown in Figure 3 by month, and total approximately 118,000 tons for the year. Although the coal-fired units represent just over 17% of total system capacity, they generate nearly 47% of the total system NO_x emissions for the year. This is a result of both higher ppm NO_x emissions and higher capacity factors for these units. The increased oil/gas NO_x emissions seen during the June - August and December - February periods reflect higher capacity factors for these units during these periods.

NO_x REDUCTION PREDICTIONS

The control techniques considered for each of the units are described below:

- ° Low Excess Air (LEA) - LEA firing involves operating the unit at a low level of total combustion air flow while maintaining acceptable flame and furnace conditions. Estimates of the reductions achievable in excess air levels ranged from 1/4% to 1% depending on unit design and operating characteristics. The reductions in NO_x levels were estimated based on interpolations developed from actual test data obtained on similar units.
- ° Burners-Out-Of-Service (BOOS) - BOOS involves terminating the fuel flow to selected burners while leaving the air registers open and the total fuel flow to the boiler unchanged. The active burners then operate with more fuel-rich stoichiometries and reduced NO_x. This technology was not considered for the coal-fired units because of the loss of operating flexibility due to the inability to use the mill feeding the out-of-service burners and the potential for unit de-rating resulting from coal feed capacity limitations of the in-service mills. For the oil and gas-fired units, a nominal level of approximately 25% BOOS was assumed for all the units. NO_x reductions were estimated using test data from similar units, interpolating to take into account differences in burner zone heat release rate and operating excess O₂ level on oil and gas, and correcting the data for different levels of fuel nitrogen in oil.
- ° Flue Gas Recirculation (FGR) - FGR involves the extraction of flue gas

from the exhaust stream and re-introducing it into the furnace by mixing it with the combustion air. Since the technique is only marginally effective with coal, it was considered only for the oil and gas-fired units. A nominal level of 15% FGR was assumed for the units considered. Since FGR is effective in reducing only the thermal component of NO_x , test data from units with similar uncontrolled levels of thermal NO_x was used to estimate reduction potential.

- BOOS + FGR - For oil and gas fired units, the reduction potential of using these two techniques together, although not additive, are complimentary. The estimate of BOOS effectiveness is the same as if the technique was applied singly. The additive effect of FGR on the thermal NO_x remaining after BOOS application was estimated using test data from units with similar levels of thermal NO_x .
- Overfire Air (OFA) - OFA operation involves operating with all burners in service at near stoichiometric conditions or slightly fuel rich with the balance of the air flow supplied through overfire airports located at an elevation above the top row of burners. For the gas and oil-fired boilers, OFA was not considered as a separate control technology since the NO_x reductions achievable with BOOS are comparable at a substantially lower cost. In cases where utilities would prefer OFA rather than BOOS in order to simplify operation or maintain full operating flexibility by not limiting the burners which can be used, the reductions predicted for BOOS can be used. The reduction potential of OFA on coal was estimated based on data reported in the literature²⁻⁵.
- Low NO_x Burners (LNB) - The gas and oil-fired burners considered were those licensed by the Japanese to U.S. boiler manufacturers, such as the Babcock-Hitachi/B&W PG-DRB burner and the Mitsubishi/C-E ROPM burner. Although there has been no installation of these burners on U.S. utility boilers, there is extensive retrofit experience in Japan, and they are offered commercially in the U.S. The estimated reductions were based on experience with the NO_x predictions and guarantees currently being made by boiler manufacturers for retrofits of the burners on a number of gas and oil-fired U.S. boilers. The LNB's considered include the combination of the burner itself, FGR, and the use of overfire air as an integral part of the low NO_x burner system. For coal units, the burners considered for the wall fired units were the B&W Dual Register Burner or the Foster Wheeler Controlled Flow/Split Flame burner with no overfire air. The PM burner with overfire air was assumed for tangentially fired units. The estimated reductions were based on data reported in the literature²⁻⁴.
- Low NO_x Concentric Firing System (LNCFS) - LNCFS is applicable to tangentially fired units, and involves directing the secondary air jet away from the fuel stream and closer to the furnace walls to delay mixing. The estimated reductions were based on data reported in the literature^{3,4} and assume the use of split buckets and air offset but not OFA.
- Selective Catalytic Reduction (SCR) - SCR is a post-combustion system in which NO_x is reduced by the injection of ammonia into the flue gas which, at proper temperature, is then processed through a fixed bed catalytic reactor. The estimated reductions were based on experience with current Japanese results and guarantees, together with the results of field tests which have been conducted at pilot facilities in the U.S. SCR was not considered as applicable to the coal-fired units in the NYPP. These units burn coal with sulfur contents in the range of 2-3%.

No applications of this technology have been reported on units burning fuels with sulfur contents greater than 1.7%. Since high fuel sulfur levels are known to have the potential to seriously degrade catalyst performance and boiler operability, the technology was judged as not commercially available for these units.

The presence of operating problems or equipment on a particular boiler which could limit the effectiveness or applicability of a control technique and which were identified during the plant visits were taken into account in estimating reduction potential. Typical unit operating or design constraints which could affect control techniques are shown on Figure 4. For example, units which experience difficulty in maintaining steam temperature generally use high levels of excess air. For these units, reducing excess air levels to control NO_x is not a viable alternative, and the control technique would not be considered as applicable. This limitation would also impact other techniques such as BOOS, which depend on low excess air levels for optimum effectiveness.

For coal-fired units, judging the applicability of any of the control techniques and assessing quantitatively the reduction potential of the technique included consideration of the following specific criteria:

- ° Unit plan area (width x depth). For tangentially-fired units, plan area rather than furnace depth is a primary concern with regard to potential flame impingement problems.
- ° Distance from the top burner elevation to the roof. In considering OFA retrofit, adequate residence time for proper mixing of the additional air with the combustion products to ensure carbon burnout is necessary.
- ° Volumetric heat release (furnace heat input/furnace volume). Large values of the parameter could indicate the potential for carbon burnout problems on OFA and LNB retrofits.
- ° Burner zone heat release (furnace heat input/burner zone cooling area). High values indicate a small furnace which results in high initial NO_x levels and limits the level to which the control technique can reduce NO_x .

An example of the estimated reduction potentials of the various control techniques from uncontrolled baseline levels is shown in Figure 5. The unit described is a 350 MWe oil-fired B&W twin furnace, natural circulation boiler. Its burner zone heat release at full load was calculated to be $0.22 \times 10^6 \text{ BTU/ft}^2 \text{ hr}$, which would be considered as average and not a limiting factor leading to high NO_x emissions. The unit is a coal conversion, and has difficulty maintaining design steam temperatures. As a result, the unit operates with relatively high levels of excess air, particularly at reduced loads, to help keep steam temperatures as high as possible. As a result of this constraint, low excess air operation was not considered to be a viable NO_x control technique. The applicable control techniques considered for the unit were flue gas recirculation (FGR), burners-out-of-service (BOOS), combined BOOS + FGR, low NO_x burners (LNB), and selective catalytic reduction (SCR). With the addition of 15% FGR to the combustion air at full load, a NO_x reduction of 23% could be expected. For 25% BOOS a 36% reduction would be predicted. Combining 25% BOOS with 15% FGR should lead to a total 48% reduction in NO_x . The predicted NO_x reduction with the installation of PG-DRB burners would be 60% from baseline, while SCR would provide 70%.

NO_x CONTROL COSTS

For each control technique, Total Capital Requirements (TCR) and Levelized Power Costs (LPC, Capital and Operating, 30 year basis), mills/kw-hr, were calculated. The economic premises used were in accordance with the EPRI Technical Assessment Guideline⁶.

Ease of Implementation (EOI) for each control was also estimated. Four criteria were used to assess this parameter: (1) Complexity of installation (amount of new ductwork required, location of control technique, integration into existing system, etc.), (2) Outage requirement, (3) Technological risk (how often controls have been implemented, length of experience with them), and (4) Potential impact on day-to-day operation. The assessment relied heavily on engineering judgement and is based on a number of qualitative criteria. In an attempt to reduce the degree of subjectivity, a weighting factor was developed for the four criteria by assigning each of them a score ranging from 1-10 (10 being the most complex to install, having the longest outage requirement, posing the largest technical risk, or having the largest potential impact on day-to-day operation. The points were then totalled, and EOI assessed by the following scale:

- ° 0-10 High EOI (easiest)
- ° 11-20 Moderate
- ° 21-30 Low
- ° 31-40 Minimal (most difficult to implement)

For the 350 MW unit, which currently operates at a 30% capacity factor unit, the following guidelines were used, costs calculated, and EOI (Criteria 1 + 2 + 3 + 4 = total) assessed:

FGR: Installation of a FGR fan, the necessary ductwork, and automatic controls.
TCR: \$2,450,000. LPC = 0.52 mills/kw - hr. EOI = 3 + 3 + 0 + 3 = 9, high.

BOOS: A \$150,000 test program to define the optimum BOOS pattern and operating conditions, assuming adequate existing plant instrumentation, no additional costs would be required. TCR \$150,000. LPC = 0.02 mills/kw - hr.
EOI = 0 + 0 + 0 + 2 = 2, high

BOOS + FGR: TCR = \$2,600,000. LPC = 0.54 mills/kw - hr.
EOI = 3 + 3 + 0 + 3 = 9, high.

LNB: Thirty two PG-DRB burners installed with new burner management system.
TCR = \$7,000,000. LPC = 1.21 mills/kw - hr. EOI = 5 + 10 + 3 + 3 = 21, low.

SCR: Complete SCR system including ammonia injection system, no site-specific installation problems, reactor located between economizer outlet and air preheater inlet. Catalyst life of two years assumed. TCR = \$30,000,000. LPC = 11.29 mills/ kw - hr. EOI = 8 + 8 + 5 + 10 = 31, minimal.

It is interesting to compare control costs in terms of their effectiveness in reducing NO_x, i.e. \$/ton NO_x removed. Figures 6 and 7 present this comparison in terms of capital required/ton of NO_x removed, and levelized annual cost/ton of NO_x removed (levelized annual cost = LPC x kw x CF x 8760). As judged by this criteria, BOOS is the most desirable control technique, followed by BOOS + FGR. LNB's despite their capital cost are quite cost effective, while SCR is disproportionately high.

Of course, the criteria of % reduction achievable is also a major factor

in the choice of a control technique. One method of comparing these controls on both a cost and % reduction basis is to look at the incremental cost required to get increasingly higher NO_x reductions (Figure 8). For increasingly stringent NO_x requirements necessitating controls beyond BOOS, the incremental increases in cost from BOOS to BOOS + FGR and from BOOS to LNB are approximately \$775/ton and \$1,380/ton, respectively. The additional cost for LNB provides the ability to obtain reductions beyond the 48% achievable with BOOS + FGR. Additional, more qualitative, considerations in deciding between which technology is more desirable for a given situation are operational factors such as the condition of the current burner system, the desirability of improving boiler reliability and thermal performance, and of operating with all burners in service. The requirement for an additional 10% reduction above that achievable with LNB's necessitates the use of SCR at an incremental cost which would seem to be very difficult to justify.

IMPLEMENTATION STRATEGY EVALUATION

For the oil- and gas-fired utility system evaluated, a comparison of the NO_x reductions and costs for each of the five implementation strategies described in Section 1.0 is presented in Table 1. For the system, the criteria of Minimum Capital Investment/Ton NO_x removed and Minimum Annual Levelized Cost/Ton NO_x removed would both be satisfied by implementing BOOS operation on all the units. This strategy would reduce total system NO_x emissions from the baseline level of 19,800 Tons/Yr by 28%. The maximum Ease of Implementation criteria would normally be satisfied by LEA operation, however, for operational reasons, this control technique is not a viable one for the evaluated system. For full load operation, excess air levels could, in fact, be reduced in order to lower NO_x levels. At reduced load, however, all of the units in the system have difficulty maintaining steam temperatures. The low capacity factors for these units (approximately 30%) are indicative of operation at reduced loads for considerable periods of time. Under these conditions, high excess air levels are required to maintain steam temperatures, with the result that LEA operation is not possible. For this reason, BOOS operation, the next easiest control to implement after LEA operation, also satisfied the maximum Ease of Implementation criteria. The strategy of maximum reduction without the use of SCR would involve the use of LNB's on all the boilers, resulting in a 55% reduction in NO_x emissions. Although the reductions are nearly double those achieved with the minimum cost criteria, the total annual cost of the strategy is nearly 50 times greater. Including SCR would provide only an additional 17% reduction over the maximum reduction without SCR case, but at 8 times the cost of LNB's.

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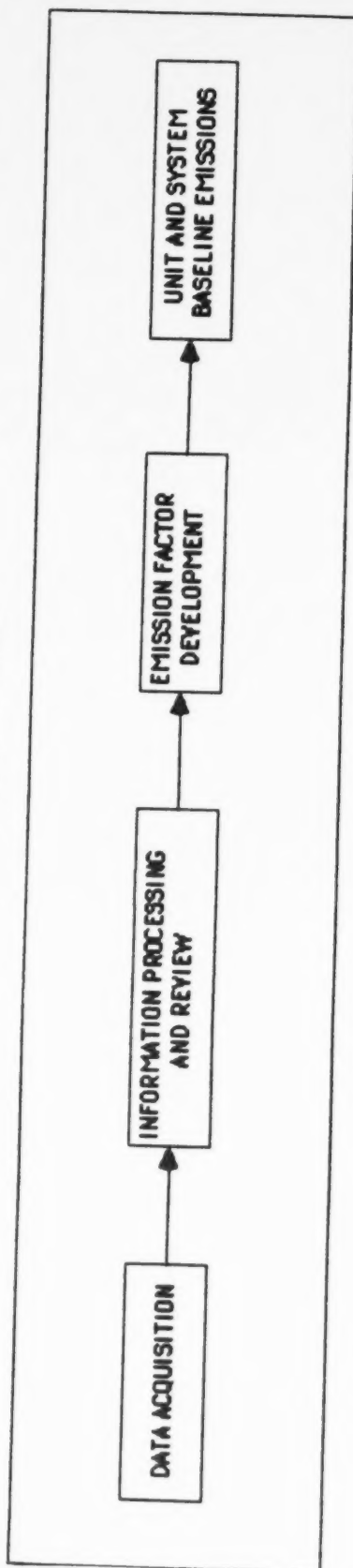
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- (5) Muzio, L. J. et al. (1983), "Control of Nitrogen Oxides: Assessment of Needs and Options, Technical Support Document", EPRI EA 2048, Volume 5.
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Implementation Criteria	NO _x Reduction Tons/Yr	NO _x Emissions Tons/Yr	TCR \$1,000	Total Annual Cost \$1,000/Yr	Annual Levelized Cost/Ton \$/Ton
Baseline	-----	19,800.	-----	-----	-----
Min. Capital Investment/Ton	5,500.	14,300.	2,700.	500.	100.
Min. Annual Level. Cost/Ton	5,500.	14,300.	2,700.	500.	100.
Ease of Imple- mentation	5,500.	14,300.	2,700.	500.	100.
Max. Reduction (No SCR)	10,900.	8,900.	117,800.	25,600.	2,400.
Max. Reduction (With SCR)	14,600.	5,200.	498,200.	220,100.	15,100.

Figures rounded to nearest hundred

TABLE 1
COMPARISON OF NO_x REDUCTION AND COSTS FOR VARIOUS IMPLEMENTATION CRITERIA
CONSOLIDATED EDISON SYSTEM

BASELINE EMISSIONS



CONTROLLED EMISSIONS

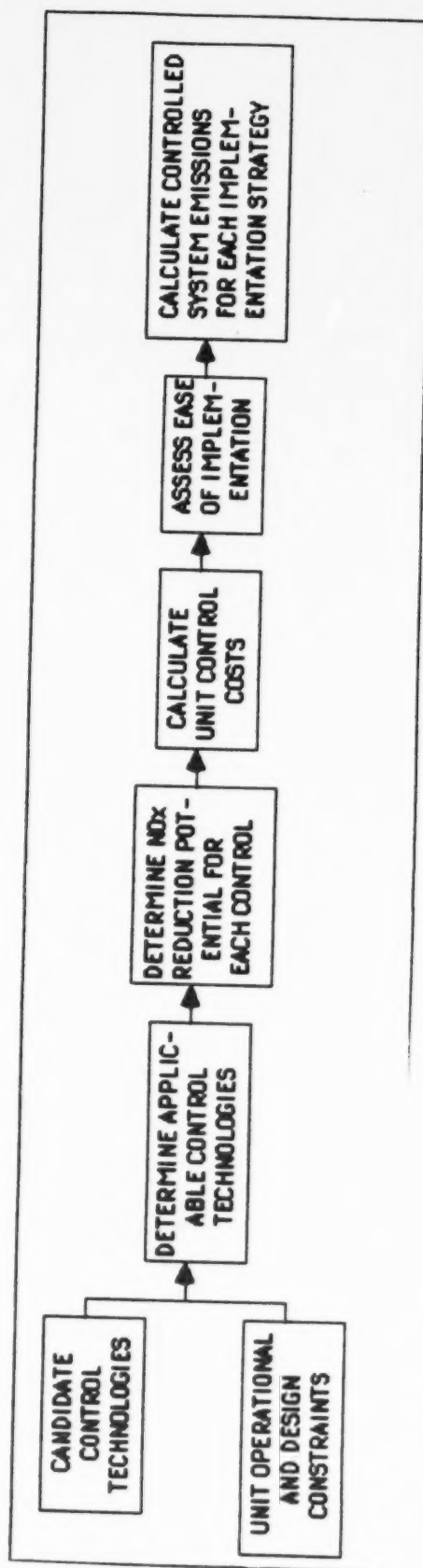


FIGURE 1 - ESEERCO PROGRAM ELEMENTS

Figure 2 - NYPP Distribution of Installed Capacity By Design Type and Fuel

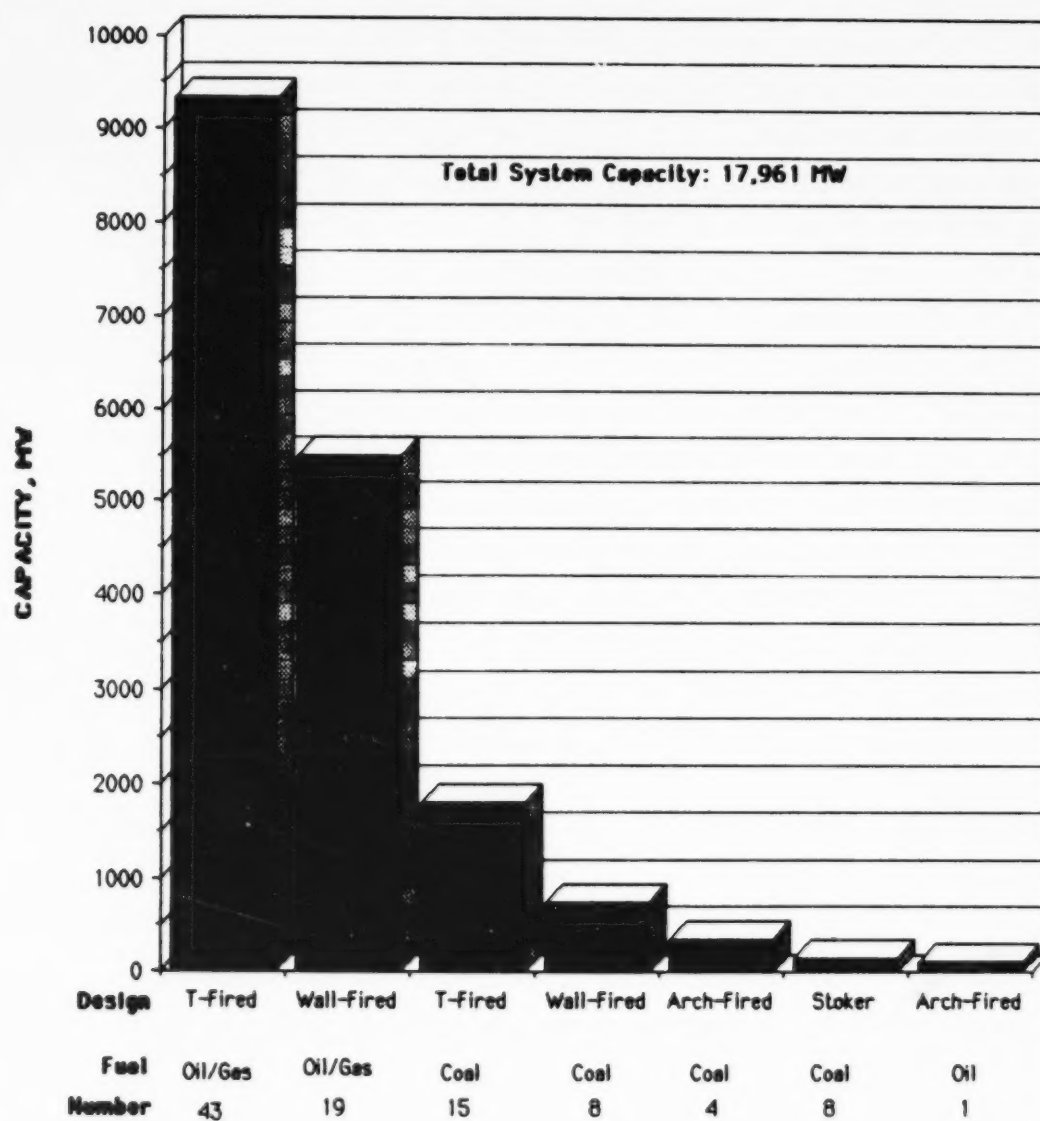


Figure 3 - 1984 NYP System Emissions

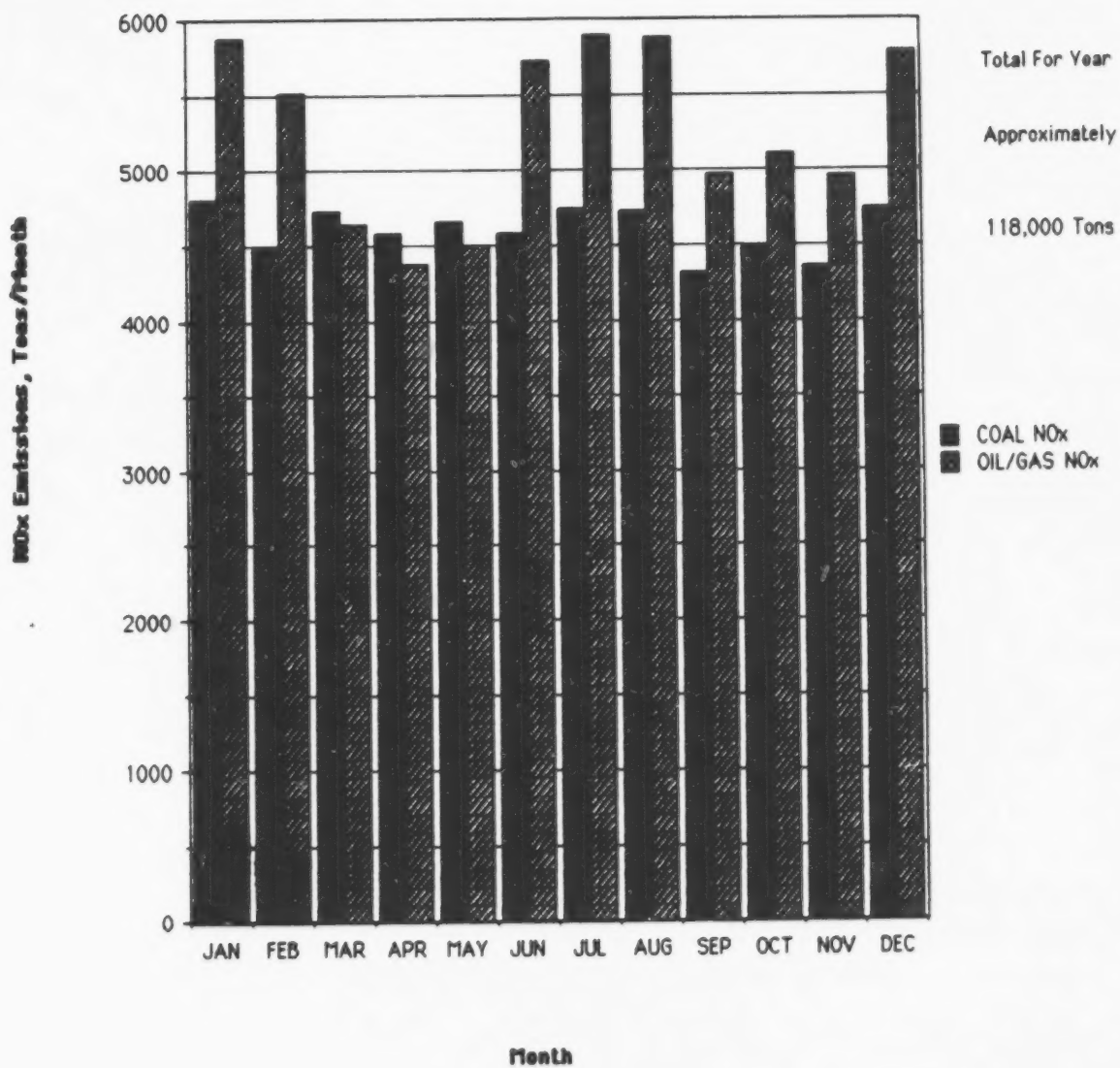


Figure 4- Typical Unit Operating/Design Constraints

CANDIDATE CONTROL TECHNOLOGIES	
o Low Excess Air (LEA)	o Burners Out Of Service (BOOS)
o Overfire Air (OFA)	o Flue Gas Recirculation (FGR)
o Low NOx Burners (LNB)	o Selective Catalytic Reduction (SCR)

UNIT OPERATIONAL CONSTRAINT	CONTROL TECHNOLOGY POTENTIALLY AFFECTED
o High attemperation	o FGR, LNB, BOOS, OFA
o Low steam temperature	o LEA
o Carbon carryover	o LNB, OFA, LEA, SCR
o Fan limitation	o FGR, BOOS, OFA, SCR
o Slagging, corrosion	o LEA, OFA, LNB, BOOS
UNIT DESIGN CONSTRAINT	CONTROL TECHNOLOGY POTENTIALLY AFFECTED
o Distance from top burner to roof	o OFA, LNB, BOOS
o Distance between burners	o BOOS
o Location of structural members, ducts, steam pipes	o OFA, LNB
o Furnace depth	o OFA, LNB, BOOS

Figure 5

350 MW Unit

Effectiveness of Various Control Technologies

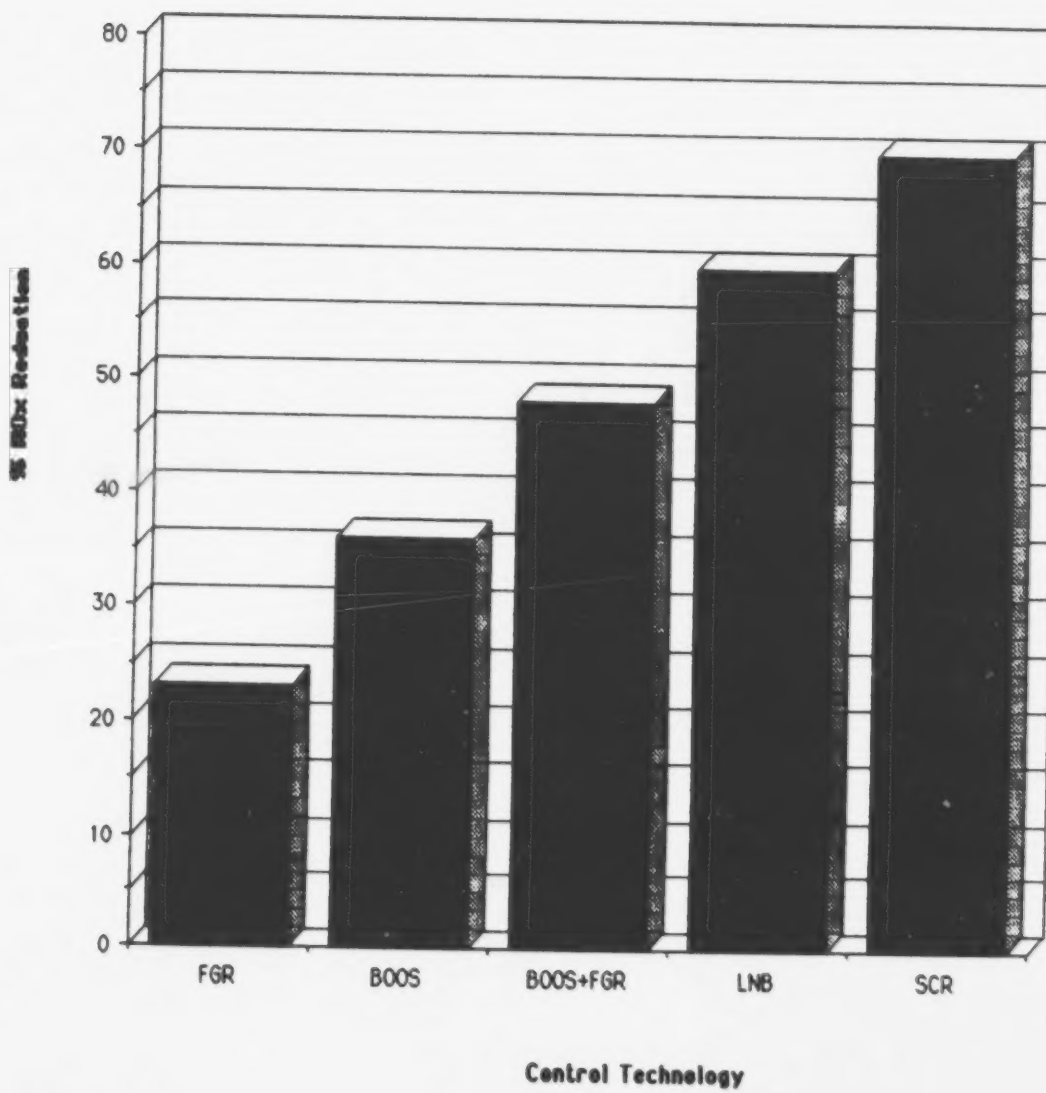


Figure 6

350 MW Unit

Control Technology Capital Costs

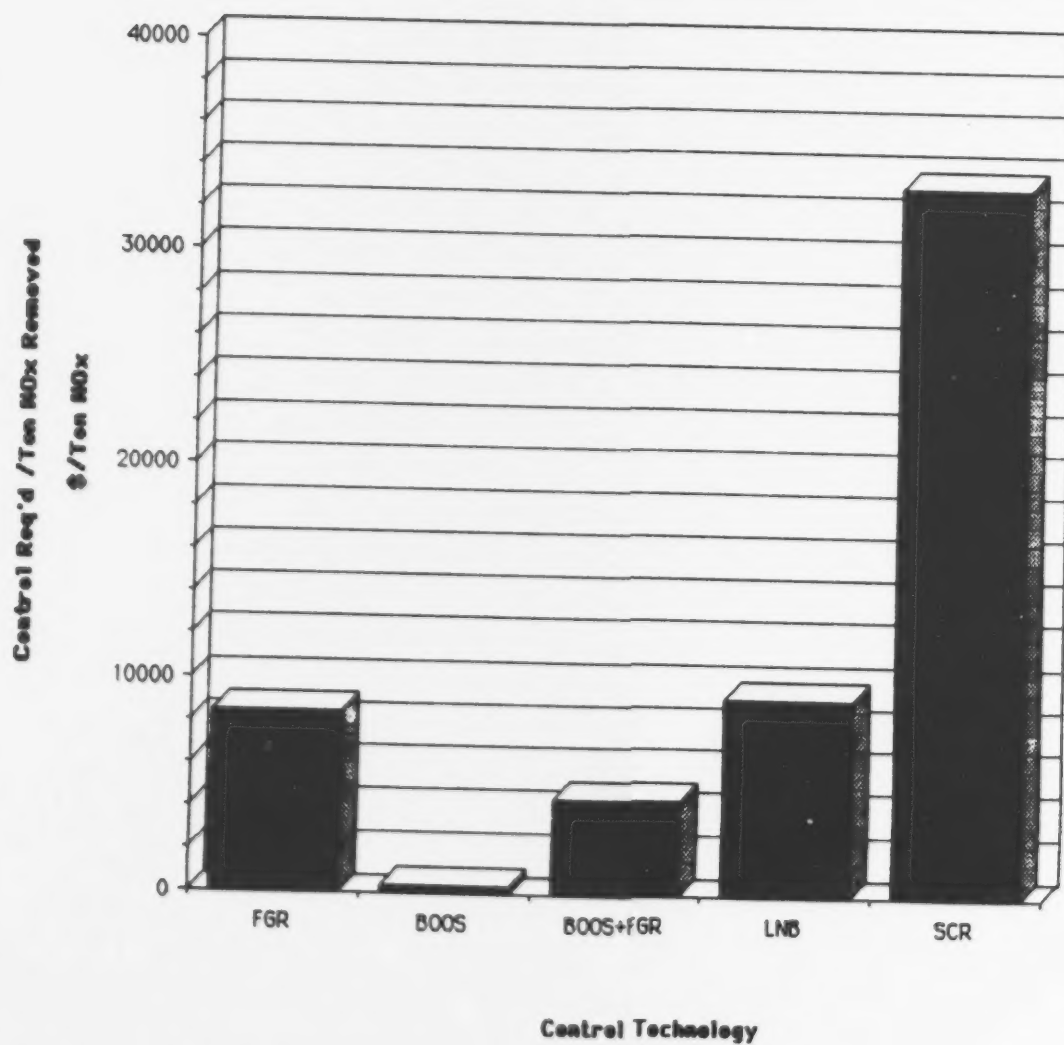


Figure 7

350 MW Unit

Control Technology Annual Levelized Costs

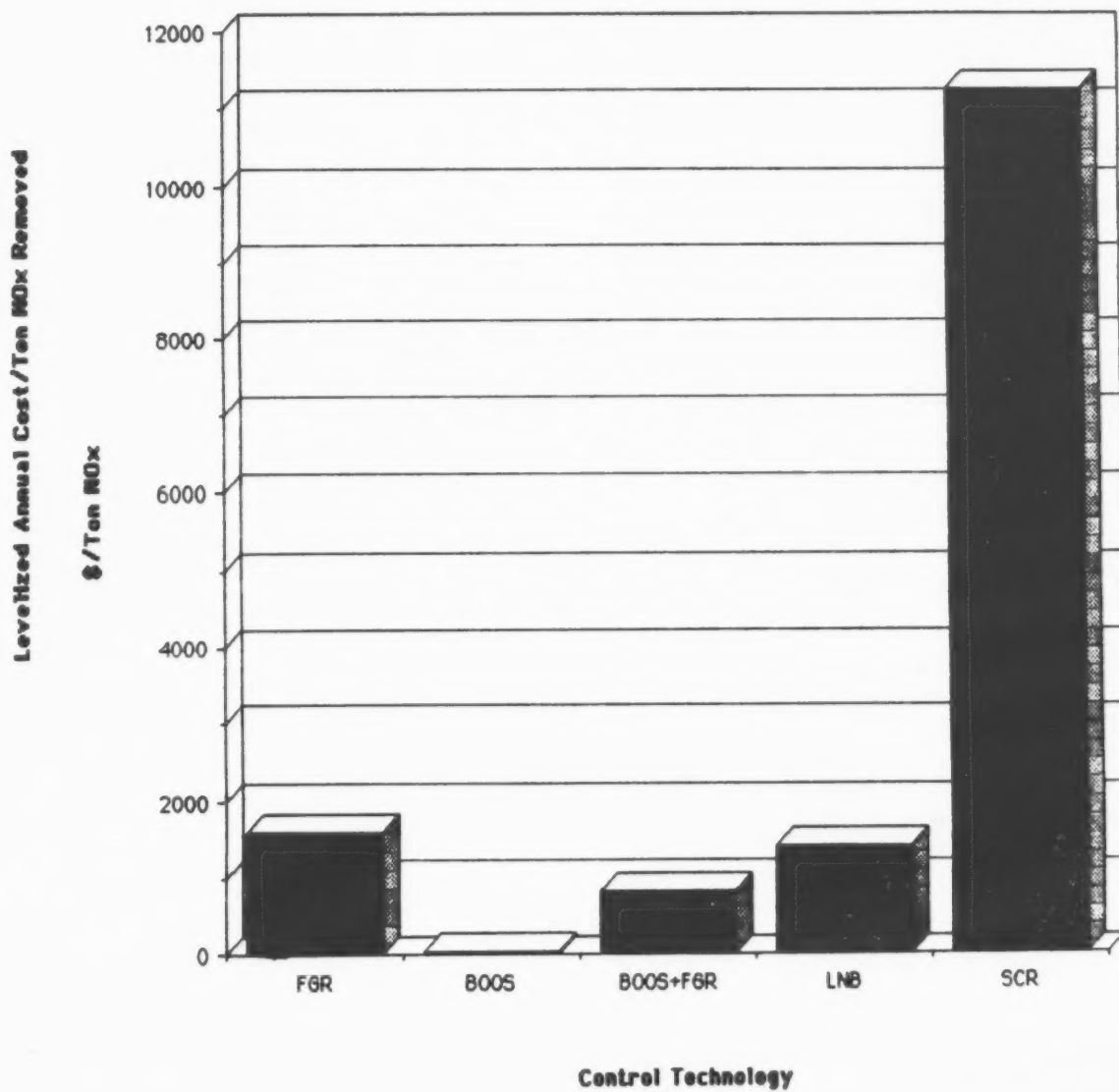
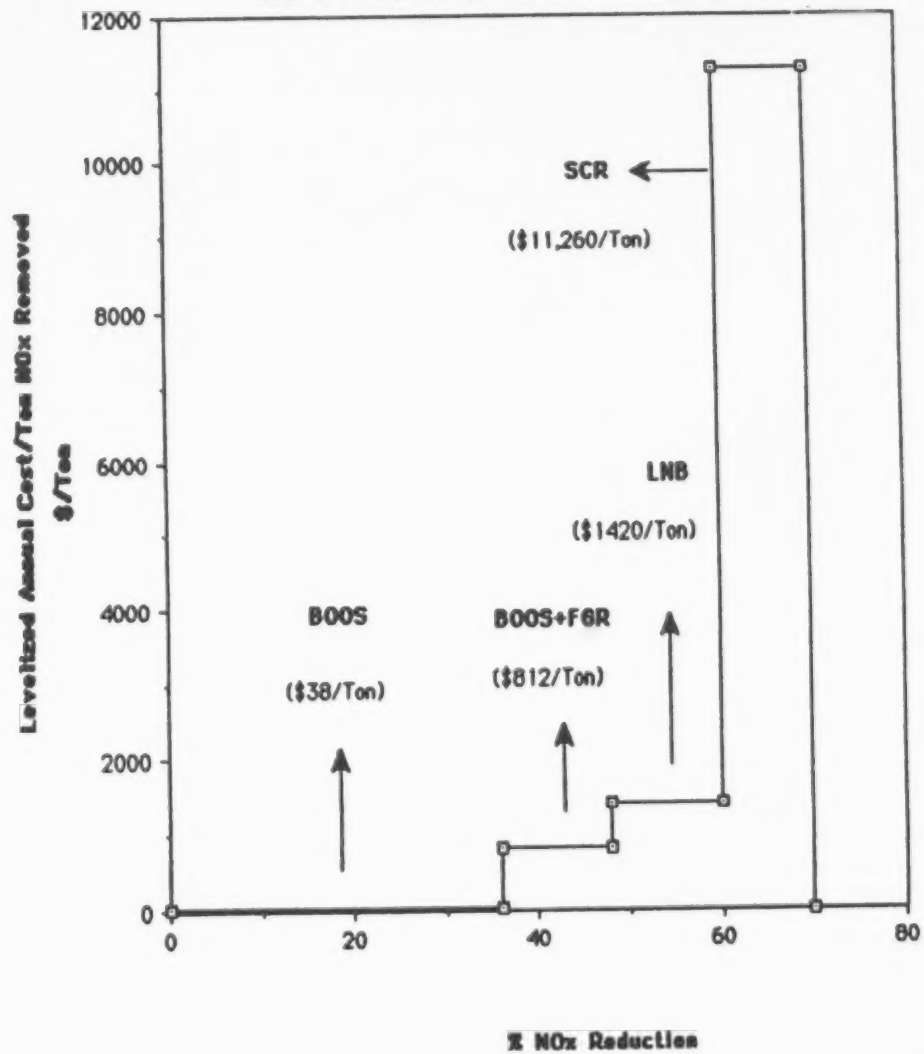


Figure 8 - 350 MW Unit

Cost For Incremental Increases in NO_x Control



FULL SCALE EVALUATION OF UREA INJECTION FOR NO REMOVAL

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ABSTRACT

An engineering evaluation was performed by San Diego Gas and Electric (SDG&E) to assess the use of urea injection for NO emissions control on gas and oil fired utility boilers. This evaluation consisted of a field assessment of the technology on Unit 2 at SDG&E Encina Generating Station and an evaluation of technology economics. The program was co-funded by Southern California Edison Company (SCE) and the Electric Power Research Institute (EPRI). Fuel Tech, Inc. (FT) co-sponsored the field assessment. The program represented the first application of the urea technology to a utility boiler.

Urea injection for NO emissions control was developed in 1976 by KVB under EPRI sponsorship. It involves spraying urea as an aqueous solution into the products of combustion where the urea reacts with NO in the gas phase to produce molecular nitrogen and water. The process is dependent on combustion gas temperature with a reduction in emissions achieved between 1400°F and 2000°F.

The results of the field assessment showed that urea is effective in reducing NO emissions from natural gas and fuel oil-fired utility boilers. NO removals ranged from 30% to 70%. Variables identified as influencing the performance of the process included the urea to NO mole ratio, injection variables, initial NO concentration, and urea solution concentration.

The economic assessment has shown that the cost of urea injection is sensitive to the level of NO removal achieved, plant size, and plant capacity factor. The total levelized costs for the process were estimated based on the performance of the system currently undergoing evaluation. The cost of the technology was estimated for plants ranging from 100 MW to 500 MW in size and operating over a broad range of initial NO concentrations. For the case studied, the levelized cost of the technology ranged from 700 to 3500 \$/ton of NO removed with the lower cost obtained for the largest plant operating at high initial NO (600 ppm @ 3% O₂).

Future work includes optimizing the performance of the urea injection system to improve reagent utilization and level of NO removal achieved. Future work will also define the control logic for a fully automated urea injection system as well as establish the effects on boiler operation of long-term urea injection.

BACKGROUND

The use of urea injection as a post combustion NO emissions control technique was developed in 1976 at the laboratory scale by KVB, Inc. (1) under the sponsorship of the Electric Power Research Institute (EPRI). The process was shown to offer up to 90% reduction in NO emissions in the laboratory. The optimum temperature window was found to be between 1800°F and 1900°F in the laboratory investigation.

In July 1985, San Diego Gas and Electric (SDG&E) initiated an engineering evaluation of the urea injection process in a full-scale gas and oil-fired utility boiler. The evaluation consisted of a field assessment of the technology on Unit 2 at SDG&E Encina Generating Station and an evaluation of technology economics. The program was co-funded by EPRI and Southern California Edison Company (SCE). The data developed during Phase I and II were used to evaluate the economic feasibility of using urea injection for NO emissions control on utility boilers.

The field assessment of the urea injection technology was co-sponsored by FT. FT has been licensed by EPRI to offer the technology commercially under the trade name NOxOUT.

The overall objective of the engineering evaluation was to assess the use of urea injection as a NO emissions control measure for gas and oil fired utility boilers. The specific program objectives consisted of the following:

- Determine the level of NO removal that can be achieved by the urea injection process during both gas and oil firing.
- Identify the effect of boiler operating conditions and urea process variables on the level of NO removal achieved.
- Identify long term operational benefits and disadvantages associated with the use of urea-injection process.

- Quantify the capital and operating cost of the process and determine its cost effectiveness.

The initial driving force for performing the program was SDG&E's desire to restore boiler operation to all-burners-in-service (ABIS) yet maintain compliance with applicable NO_x emissions regulations. Additional benefits identified for using the technology included the following:

- Eliminate or minimize the use of combustion modification techniques for NO emissions control and thus improve boiler efficiency. These techniques include flue gas recirculation, burners-out-of-service, and over-fire air ports.
- Eliminate or minimize the use of fuel oil additives generally required to control carbon or smoke emissions and thus reduce operating costs.

PROCESS DESCRIPTION

Urea is sprayed into the combustion gas as an aqueous solution. NO reduction was shown in the field to occur at a temperature between 1400°F and 2000°F . The chemical can be purchased in three forms; prilled, granular, and aqueous solution. The properties of these compounds are summarized in Table 1. Urea represents a household product that is used as a fertilizer. No special safety precautions are required for the handling of the chemical. Obtaining the urea in the form of an aqueous solution eliminates the need for on-site mixing of solid urea in water.

The details of the chemistry of the urea reaction with NO is not known. It is believed that urea thermocracking and decomposition leads to the production of NH_3 species which reduce NO to N_2 and H_2O . Based on urea chemical composition, it has been assumed that two moles of NH_2 are produced per mole of urea.

Salamian and Hanson (2) developed a NH_3 - NO kinetic model to predict the sensitivity of urea/ NO reaction to temperature and to define the temperature level for maximum NO removal. Using the model, they have calculated the effect of injecting 300 ppm of NH_2 and 150 ppm of CO on NO removal in a combustion gas mixture containing 300 ppm of NO . The composition selected assumed that urea decomposes to two moles of NH_2 and one mole of CO . The gas composition used therefore simulated a NO to urea mole ratio of 0.5.

The calculated results showed that the peak efficiency of NO removal using urea is comparable with NH_3 injection but the reaction time is shorter. In addition, the results showed that optimum temperature for the urea reaction with NO should be obtained at 1110°F . This result was inconsistent with the data obtained in the laboratory and at full-scale which showed optimum performance to occur at higher temperatures. This indicated that urea dissociation does not necessarily result in the direct production of NH_2 and a more complex chemistry is involved in the urea reduction of NO .

PROCESS VARIABLES

The performance of the urea injection process is influenced by the physical as well as the chemical processes associated with the release of the NO reducing species. As discussed above, urea is sprayed into

the furnace as an aqueous solution. The initial evaporation of the water causes the urea to remain at 212°F which is below its dissociation temperature. When the concentration of urea reaches saturation, the reagent superheats and dissociates producing NO reducing species. This evaporation/dissociation process produces a delay in urea dissociation until it is well dispersed within the furnace. Such delay can be controlled by varying the concentration of urea in solution and by varying the degree of reagent atomization. As expected, a reduction in the initial urea concentration increases the amount of water that must evaporate before urea concentration in solution reaches saturation. This increases the delay period leading to urea dissociation. In a similar manner, an increase in drop size for the aqueous solution increases the evaporation time of the drop and in turn the delay for urea dissociation.

Urea concentration and the drop size of reagent spray also influence, in a mechanical sense, the dispersion of urea within the furnace. For a given reagent injection rate, reducing the urea concentration in solution increases the mass of the aqueous solution injected. This increases the momentum of the injected spray and its penetration and mixing within the furnace. Increasing the drop size of the aqueous solution also increases the momentum of the spray allowing improved dispersion of the chemical within the furnace.

Chemical factors that influence the performance of the urea process are related to the complex chemistry associated with urea dissociation and the concentration of the reacting compounds. A high initial NO concentration and/or a low urea injection rate invariably enhances urea utilization. This is due to an increase in NO concentration relative to urea.

The physical and chemical processes associated with the urea reaction with NO result in a set of variables that influence the process performance. The most important of these variables are the following:

PROCESS VARIABLES

- NO to urea mole ratio;
- Injection variables: type of atomizer, injection location, and atomization quality;
- Initial NO concentration;
- Urea concentration in solution.

OPERATIONAL VARIABLES

Operational variables can influence the combustion gas temperature at the urea injection location and the initial NO concentration and therefore have an effect on the level of NO removal. The most important of these variables are:

- Fuel type (natural gas or fuel oil);
- Boiler load;
- Burner firing pattern;

- Windbox or hopper flue gas recirculation;
- Furnace excess O₂.

TEST EQUIPMENT AND SCOPE OF TESTING

TEST EQUIPMENT

The program was performed on SDG&E Encina Unit #2; a front wall fired boiler built by Babcock and Wilcox. A boiler side cross-section is presented in Figure 1. The boiler operates with a balanced draft furnace and is equipped with two vertical-shaft Ljungstrom regenerative air preheaters. Ten burners, arranged in two elevations with five burners in each elevation, provide the heat input to the boiler. The burners are manufactured by Peabody and can be fired on natural gas as well as fuel oil.

Urea was supplied to the boiler by a skid mounted injection system designed and built by FT specifically for the field assessment. The urea was delivered in the form of an aqueous solution with a 50% urea concentration. The injection skid incorporated four variable speed gear pumps to modulate urea flow at the desired level. A separate pump supplied dilution water to change urea concentration in the solution as it was injected into the furnace. The water and the concentrated urea solution were mixed in a static mixer. Instrumentation was incorporated into the injection skid to monitor the flow of all streams.

Several atomizer designs were examined to optimize the performance of the process. However, the data presented in this technical paper are limited to the two types of atomizers that provided the best performance. The first atomizer, referred to herein as Atomizer A represents an external twin fluid atomizer developed by FT. The second atomizer, referred to as Atomizer B was a conventional y-jet twin fluid atomizer. The A atomizers were installed through the boiler front wall using Ports 1-7 as designated in Figure 1. The B atomizers were installed through Ports A and B. The gaseous species were measured at the inlet to the air preheater (Figure 1).

Figure 2 provides an isometric drawing showing the position of the atomizers in relation to the boiler convective section and flame basket. As presented in this figure, the A atomizers injected the reagent toward the screen tube (superheater section) and each injection probe contained one atomizer. The B atomizers injected the reagent away from the screen tube counter to the flow of the combustion gas. For Atomizer B, two probes were used and each probe contained four atomizers. The rotation of the probe assembly around its axis (Figure 2) down toward the boiler flame basket or up toward the furnace top provided some flexibility in altering the combustion gas temperature at the location of injection.

SCOPE OF TESTING

Testing was performed to determine the effect of operating conditions and process variables on NO removal achieved. Boiler operating conditions considered included load and fuel type (gas or oil). Process variables examined included urea to NO mole ratio, injection variables, initial NO concentration, and urea concentration in solution.

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Urea utilization was selected as the performance criteria since this parameter provided an accurate indication of the efficiency of the process. The urea utilization was defined as the moles of urea, on a percent basis, that reacted with the NO contained in the combustion gas. The term Normalized Stoichiometric Ratio (NSR) was developed to describe the urea to NO mole ratio. The NSR was defined as follows:

$$\text{NSR} = \frac{\text{Actual Molar Ratio of Urea to Initial NO}}{\text{Stoichiometric Molar Ratio of Urea to Initial NO}}$$

The stoichiometric molar ratio was equivalent to having a urea to NO mole ratio of 0.5 since there are two moles of NH_3 contained in each mole of urea.

The NSR provided a dimensionless parameter that describes the relative amount of reagent injected. A NSR greater than 1.0 would indicate that injected urea is in excess of NO contained in the combustion gas. Theoretically, a NSR of 1.0 would provide a 100% NO removal. This can be only be achieved, however, if the mixing and utilization of reagent are 100% efficient.

Continuous emissions monitoring was conducted to determine NO, NO_x , CO, and O_2 concentrations in the stack gas. These measurements were provided by the SDG&E Environmental Analysis Section staff. Composite gas samples were obtained in the ducting to provide an integrated sample of the gas composition. For selected tests, gaseous species profiles were determined to examine the efficiency of urea mixing with combustion gas. Grab samples were also obtained during oil firing, for selected tests, to determine SO_x , NH_3 , and HCN concentrations in the stack gas. A few tests were also performed to determine the presence of nitrosoamines in the stack gas.

UREA INJECTION SYSTEM DESIGN

Achieving the proper mixing of urea at the optimum combustion gas temperature represented a major requirement for the successful performance of the urea process. To address this requirement, furnace probing was performed across certain boiler elevations to select the location most suited for the injection of the urea and to determine the combustion gas temperature profile at the urea injection location. Furnace probing was also performed to measure gas velocity to determine furnace flow characteristics and thereby optimize reagent mixing.

The combustion gas temperature was measured by a multiple-shield high velocity temperature probe. This probe is designed to minimize errors associated with heat loss by radiation and conduction, providing temperature measurements that approach the actual gas temperature. The temperature measurements were made across the furnace cavity as well as at the inlet to the screen tube (superheat section) while operating the boiler with ABIS.

The range for combustion gas temperature measured as a function of boiler load is presented in Figure 3 for both natural gas and fuel oil firing. These data show that at the same elevation, the spread in temperature measured ranges from a minimum of 350°F to a maximum of 665°F. The data thus indicated that severe stratification in combustion gas temperature profile exists at the urea injection location. This temperature stratification was less pronounced for oil firing suggesting that improved process performance would be obtained during

fuel oil combustion. The spread in measured temperature values increased with load for fuel oil firing but remained essentially unchanged for natural gas firing. At the chosen injection location, a boiler load of 80 MW appeared to offer the most favorable temperature conditions for the injection of urea.

A three-dimensional plot of the combustion gas temperature profile obtained at 110 MW during gas firing is presented in Figure 4. The plot represents a sample of temperature measurements made at other loads and for other fuels. As can be seen in this figure, the gas temperature near the boiler wall is lower than the inner portion of the furnace, reflecting the cooling effect of the furnace walls. In addition, lower temperatures are measured in the furnace center suggesting the presence of a gas recirculation zone carrying the combustion gas along the furnace wall to the center of the furnace.

Velocity measurements were made at the furnace exit and at the inlet to the screen tubes. As with the temperature data, the spread in velocity measured at the same plane within the furnace varied over a broad range. The data supported the possible presence of gas recirculation fields within the furnace. A sketch of these recirculation fields is presented in Figure 5. It is believed that the recirculation was caused by a negative pressure zone in the center of the furnace. This appeared to create vertical as well as horizontal vortices (Figure 5) which carried furnace gas from along the side of the furnace walls to the center of the furnace.

The furnace probing provided important information on combustion gas temperature profiles and flow characteristics. These data allowed the selection of the urea injection location and the optimization of process performance. In developing the B atomizers, the injection system was designed to take advantage of the furnace recirculation zones and improve reagent mixing with the combustion gas. It is therefore felt that furnace probing is a necessary step in implementing the urea injection technology.

SELECTION OF ATOMIZER CONFIGURATIONS AND LOCATION OF UREA INJECTION

Atomizer designs and injection probe configurations and locations were screened to identify the injection system design that would provide maximum NO removal. The data presented in this paper were obtained with two atomizer designs that provided the best performance (Atomizers A and B). In this demonstration, Atomizer B offered an improvement in process performance over Atomizer A. This was due to the positioning of the Atomizer B injectors to take advantage of furnace recirculation zones and the performance of the atomizer itself, which enhanced the penetration and mixing of the reagent spray. Unfortunately, due to the fact that Atomizer B was developed near the end of Phase II, all data with oil firing were obtained with Atomizer A while data for gas firing were obtained with Atomizer B. This fact complicates the comparison of process performance with gas and oil firing. It did offer an opportunity, however, to show that injection parameters are a dominant factor in determining process performance. NO removal for gas firing using Atomizer B was comparable to that of oil in spite of the low initial NO and unfavorable combustion gas temperature associated with gas firing. Future plans involve a more extensive evaluation of Atomizer B during both oil and gas firing.

Atomizer B was tested in two operating modes. In the first mode (Atomizer B1), the urea and atomizing gas supply were connected to provide good atomization quality using the standard configuration for

a y-jet atomizer. In the second mode (Atomizer B2) the atomizer porting was modified to provide coarse urea atomization at high atomizing gas pressures. The coarse spray and large quantity of atomizing gas used increased the discharge momentum of the reagent and enhanced the urea penetration and mixing.

EFFECT OF INJECTION PARAMETERS

Injection parameters include the atomizer type, injector location, atomizing medium pressure, and mass of injected reagent. The effect of atomizing medium pressure on atomization quality is a function of atomizer design. Generally, high atomization pressure provides improved atomization which promotes the early release of urea to react with NO. In Atomizer B2, however, an increase in atomizing medium pressure did not result in a measurable improvement in atomization but did increase the discharge momentum of the reagent. This improved the reagent penetration and mixing and, in turn, the process performance.

For a given NSR, reagent mass flow can be varied by changing urea concentration. Reduced urea concentration increases the mass throughput of the reagent and thus its penetration and mixing. For a twin fluid atomizer, similar to Atomizers A and B, an increase in reagent flow would also result in a deterioration in atomization quality. This leads to a larger momentum for the atomized spray and improved mixing.

The effect of injection parameters on the performance of the urea process is presented in Figures 6 through 8. Figure 6 illustrates the impact of injector design on urea utilization. The data presented in this figure compare the performance of Atomizers A, B1, and B2 at 80 MW load during gas firing. These data show that injector design has a significant effect on reagent utilization. For example, at a NSR of 2.0, the reagent utilization for the Atomizer B2 was in the range of 33%. The utilization for the Atomizer A was only 14%. This shows that atomizer design resulted in a 135% improvement in utilization.

Maximum utilization was obtained with Atomizer B2 due to both the injection location and the design of the atomizer. The injector location offered improved mixing of the reagent by taking advantage of furnace recirculation zones. The atomizer design allowed the use of large amounts of atomizing medium without measurably improving atomization. This increased the momentum of the reagent spray and in turn its ability to penetrate and mix with the combustion gas.

Figures 7 and 8 show the effect of injection momentum on utilization. Figure 7 illustrates the effect of increasing the injection momentum by increasing reagent throughput to the boiler. This was achieved by reducing urea concentration and thus the amount of aqueous solution injected into the furnace at a given NSR. The data are presented for 80 MW and 110 MW boiler loads when firing fuel oil. The data were developed using Atomizer A.

As can be seen in Figure 7, increasing the mass of the reagent throughput to the boiler increases the urea utilization. This is attributed primarily to the improved mixing of the reagent with combustion gas achieved by the increase in injection momentum and spray drop size. The low urea concentration also delays the release of the urea since more water must evaporate before the urea concentration in the solution reaches saturation. The improved mixing and increased delay in urea release allowed a longer residence time for the reagent to disperse. In these tests, higher utilizations, at

fixed NSR values, were obtained at 110 MW due to the higher initial NO concentration.

Figure 8 further illustrates how reagent penetration and mixing can affect utilization. As can be seen in this figure, Atomizer B was used in two operating modes (B1 and B2). The tests were performed with increasing atomizing medium pressures for both atomizer configurations to determine the change in reagent utilization.

In the case of Atomizer B1, increasing atomizing medium pressure improved atomization quality. This hindered the penetration and mixing of the reagent and in turn reduced reagent utilization. In contrast, increasing the atomizing medium pressure in Atomizer B2 increased the discharge momentum of the reagent spray. This initially increased reagent utilization due to improved mixing. Increasing atomization pressure beyond a certain point began to improve atomization, however, and enhanced the early release of urea. It is believed that the competing effects of increased reagent momentum and improved atomization quality thus resulted in little or no change in utilization as atomization pressure was increased beyond a certain point.

NO REMOVAL

The NO removal efficiency achieved for two boiler loads is illustrated in Figures 9 and 10. These data present several important results. The first is that a NO removal in the range of 30% to 70% can be achieved with the use of urea injection at a NSR value ranging between 1.0 and 2.0. Based on the combustion gas temperature profile data and the NO removals achieved, the data appeared to indicate that the process is not as sensitive to combustion gas temperature as was originally believed based on the results obtained in the laboratory.

Data obtained at 80 MW load for gas and oil firing (Figure 9) provided a comparable NO removal efficiency even though the initial NO for natural gas firing was 150 ppm (corrected to 3% O₂) and for fuel oil firing was 240 ppm (corrected to 3% O₂). Furthermore, comparable NO removal was obtained for the two fuels in spite of the unfavorable combustion gas temperature and temperature profile obtained by natural gas firing. The result thus suggested that unfavorable urea injection conditions (high temperature and/or low initial NO) can be offset by optimizing the design of the urea injection system.

NO removal obtained during oil firing was higher than that achieved during gas firing at 110 MW load. (Figure 10). This was primarily attributed to a more favorable combustion gas temperature and higher initial NO concentration obtained by oil firing at this load. The gas data were obtained using Atomizer B1. It is expected that improved performance will be achieved when using Atomizer B2 showing that atomizer design can compensate for adverse operating conditions. Such testing will be performed in the forthcoming phase of the field evaluation.

The effect of initial NO concentration on NO removal was not fully investigated during the field evaluation. Variations in initial NO tested were within a narrow range (150 - 300 ppm @ 3% O₂). Based on laboratory results it is expected that higher NO removal will be obtained with an increase in initial NO concentration (Figure 11). The increased removal will be noted only with large variations in initial NO concentration. Based on the data obtained in the laboratory, it is therefore believed that the performance of the urea process will improve when applied to applications with high initial NO

concentration. These include cyclone fired boilers, boilers operated on high sulfur/nitrogen fuel oil, and coal fired boilers.

The data showed that increased NO removal with increasing NSR can reach a point of diminishing return. At this point, a further increase in NSR results in a very modest or no increase in NO removal. This is due to a decrease in reagent utilization which offsets the increase in the amount of reagent used. The data thus suggest that high reagent utilization must be maintained in order to achieve increased NO removal at high NSR values.

The change in urea utilization as a function of NSR is presented in Figures 12 and 13. As implied by the NO_x removal data, the data clearly illustrate that reagent utilization does drop with the increase in NSR. This drop in utilization is related to chemical and mixing factors. At low NSR values, the concentration of NO relative to urea is large. This enhances the reaction rate and results in improved reagent utilization. As the amount of reagent injected is increased, it becomes increasingly difficult to disperse the reagent efficiently. In addition, the relative concentration of the reacting compounds becomes more balanced reducing the rate of reaction between NO and urea. The combined effect of these two factors is a reduction in reagent utilization. As the NSR value exceeds 1.0, a surplus of reagent becomes available resulting in inefficient use of the reagent.

Achieving high urea utilization is very critical to process performance. A 10% increase in utilization at a NSR of 2.0 will result in 20% increase in NO removal. Therefore more emphasis should be placed during future development on improving utilization especially at high NSR values.

The performance of the urea injection process was not examined during this program at very low boiler loads (<50%). Based on limited field data and results obtained in the laboratory, the effectiveness of the process is expected to be limited. This is due to very low combustion gas temperature that would occur at the urea injection location with the reduction in boiler load.

OTHER EMISSIONS

Testing was performed during the course of the program to determine the effect of urea injection on other air emissions. These included NH₃, HCN, nitrosoamines and CO. NH₃ and HCN were determined using standard wet chemistry techniques. Nitrosoamines were measured by gas chromatography using sampling techniques developed by SCE and Radian Corporation. CO was measured by continuous emission monitoring using SDG&E emissions van. The data were obtained during oil firing using Atomizer A.

The result of these tests showed that NH₃ is a byproduct of urea injection. NH₃ emissions versus NSR are presented in Figure 14. These data represent all the NH₃ measurements obtained during the evaluation and cover a broad range of operating and test conditions. The data showed an increase in NH₃ emissions with an increase in NSR. The data also showed that for a NSR of 1.0, NH₃ ranged from 10 ppm to 50 ppm. During these tests, the injection variables were not optimized to reduce NH₃ emissions. Efforts presently underway to improve reagent utilization (use of Atomizer B2, for example) are expected to further reduce NH₃ emissions.

No detectible HCN or nitrosoamines were measured in stack gas as a result of urea injection. CO emissions increased on the average between 60 and 80 ppm. These results led to the conclusion that those emissions do not represent a concern when using the urea process.

ECONOMICS OF UREA INJECTION PROCESS

Based on the data developed during this field assessment, an economic evaluation of the urea injection technology was performed. This evaluation was made in accordance with EPRI Technology Assessment Guidelines (3). The economic premise used in performing the evaluation is summarized in Table 2. The results of the economic evaluation are considered preliminary at this time. The evaluation determined the levelized cost of emissions reduction in mills/kW-hr and \$/ton of NO removed.

The levelized cost of NO removal with the use of urea injection assuming a 100% plant capacity factor ranged between 0.34 and 2.71 mills/kW-hr and between 700 and 3500 \$/ton of NO reduced. The economic assumptions (Table 2) resulted in a levelization factor of 2.314. Unlevelized values can therefore be obtained by dividing the levelized values by 2.314.

Factors which influenced the cost of the technology included plant size, initial NO concentration, and level of NO removal. The analysis was performed for three plant sizes; 100 MW, 300 MW, and 500 MW and for a range of initial NO concentrations between 200 and 600 ppm (@ 3% O₂). Four NSR values were considered; 0.5, 1.0, 1.5, and 2.0. The NO removals achieved were based on the data obtained in the field demonstration. The cost analysis assumed the supply of the urea was in the form of a 50% aqueous solution which was found to be more cost effective than the on-site mixing of solid urea in water. All cost data did not include the cost of the licensing fees.

To determine the cost of the technology, the capital cost of the urea injection system, and the cost of the system per kW of generation were determined. A summary of this cost data is contained in Table 3. The cost of the urea injection system did not substantially change with an increase in plant capacity. This caused the cost per kilowatt of generation to drop as plant capacity increased.

A case study was performed to determine the levelized cost of emissions reduction (\$/ton of NO reduced) as a function of plant capacity factor. In this analysis, it was assumed that the capability factor represents the number of hours, on a percent basis, the boiler is operated at its full rated capacity. This is not an accurate indication of plant capacity since a low capacity factor may also mean that the boiler is operated all year round at reduced load. This assumption was made however to simplify the analysis.

The results of this study are presented in Figures 15 and 16. The study was performed for a 300 MW plant assuming a 300 ppm (@ 3% O₂) initial NO concentration and a NSR of 2.0. Based on the field data, these conditions provided a 60% NO removal. The case study showed that the levelized cost of NO emissions removal for the above conditions ranges between \$1,600 and \$2,000 per ton of NO removed (Figure 15). The actual cost depends upon plant capacity factor, with lower costs achieved at high capacity factors. The cost of emissions reduction did not substantially change with plant capacity factor due to the relatively low capital cost for the urea injection system. The operating and maintenance costs consisting of reagent cost,

electricity, and labor, represented the major portion of the cost of emissions reduction.

The cost of emissions reduction appeared to be a complex function of the level of NO removal achieved or NSR. The change in NO emissions removal cost for a range of NSRs and for different capacity factors was examined in the case study and is illustrated in Figure 16. Intuitively one would expect the cost of NO removal to be low at low NSR values due to the improvement in reagent utilization (Figures 12 and 13). However, other costs pertaining to the capital cost and labor charges become dominant when the total tons of NO removed is reduced (low NSR values). This causes the cost of the technology to drop to minimum at NSR values in the range of 1.0 to 1.5. For NSR values in excess of 1.5, the decreased reagent utilization leads to a modest increase in the cost of emissions reduction.

CONCLUSIONS

The data contained in this paper represent the first application of the urea injection technology to a gas and oil fired utility boiler. The results presented are therefore to some extent boiler-specific. The field data were for the most part consistent with the laboratory results with comparable NO removals obtained at the same NSR values. This result suggested that laboratory investigation can be effective in optimizing process performance. The field data have allowed certain general conclusions to be reached which are discussed in this section.

- Urea injection represents a technology for controlling NO emissions from natural gas and fuel oil fired utility boilers that can be used to maintain compliance with emissions regulations;
- The implementation of urea injection may offer additional benefits. These may include:
 - eliminate or minimize the use of combustion modification techniques for NO emissions control. These techniques include flue gas recirculation, burners-out-of-service, and overfire air ports;
 - eliminate or minimize the use of fuel oil additives generally required to control carbon or smoke emissions and thus reduce operating cost;
- Reagent injection parameters represent the most important criteria for achieving satisfactory process performance. Optimizing the injection parameters can compensate for unfavorable operating conditions such as low initial NO concentration and/or high combustion gas temperature. In general, coarse atomization and high discharge momentum of the reagent spray provide optimum performance.
- Level of NO removal achieved is dependent upon the amount of urea injected (NSR). A point of diminishing return is reached however where an increase in NSR results in little or no increase in NO removal. This is the result of poor reagent utilization at high NSR values.

- Reagent utilization especially at high NSR values is critical for achieving high NO removal. In addition to improving process performance, high reagent utilization is expected to reduce NH₃ emissions.
- Combustion gas temperature and initial NO concentration are believed to be important process variables. The process dependence on temperature however is not as critical as was originally believed based on the laboratory data.
- The performance of the urea injection process was not examined at very low boiler loads (<50%). Based on limited field data and results obtained in the laboratory, the effectiveness of the process is expected to be limited. This is due to very low combustion gas temperature that would occur at the urea injection location with the reduction in boiler load.
- Furnace probing to determine combustion gas temperature and velocity profile is a necessary step to select the injection location and optimize reagent mixing with combustion gas.
- For cases studied, the levelized cost of NO removal ranged between 700 and 3500 \$/ton of NO_x reduced.

FUTURE WORK

The formation of ammonium bisulfate and the deposition of this material on the air preheater over an extended period of time has caused severe fouling in other post combustion treatment techniques using NH₃ injection for NO emissions control. The air preheater fouling was experienced only when these techniques were applied to boilers burning sulfur bearing fuels. The formation of ammonium bisulfate has been related to the reaction of NH₃ contained in the stack gas with SO₃.

Since NH₃ was produced as a result of urea injection, an evaluation will be performed in Phase III to determine the impact of urea injection on air preheater fouling. This evaluation will be made over an extended period of time with oil firing to document the compounding effect of bisulfate deposition.

As discussed above, reagent injection parameters represent the most important criteria for achieving high utilization. Therefore further optimization of injection system design is planned for Phase III. In addition, work will be performed to determine the control logic for a urea injection system to allow system operation in the automatic mode.

ACKNOWLEDGEMENT

The authors wish to acknowledge the technical support of the staff of the Encina Power Plant headed by Mr. Harry Stoehr. Without their diligent cooperation, this demonstration would not have been possible. The authors also wish to acknowledge the support of the SDG&E Environmental Analysis Section for the performance of air emission measurements and the Environmental Affairs Section for obtaining the necessary permits to perform this demonstration.

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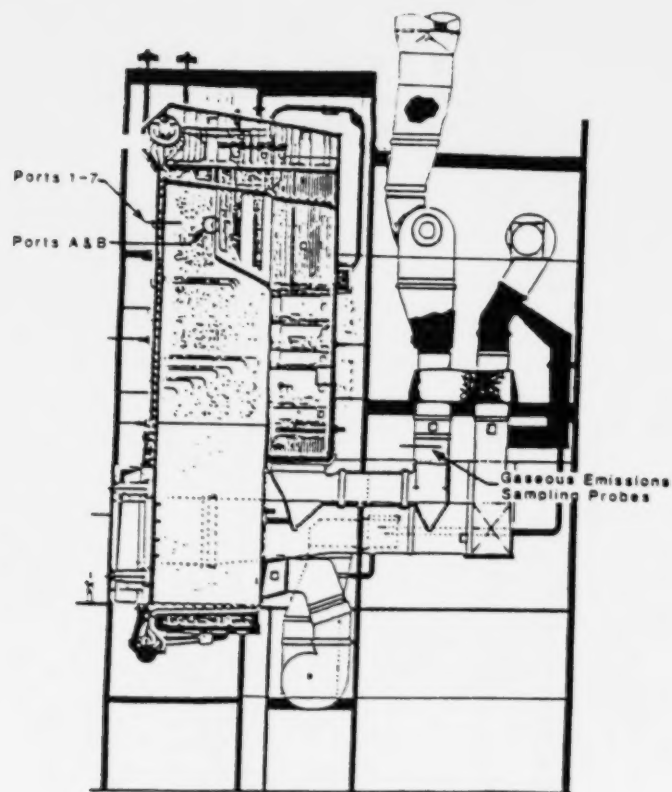


Figure 1. Encina Unit 2 Boiler Side Cross-Section

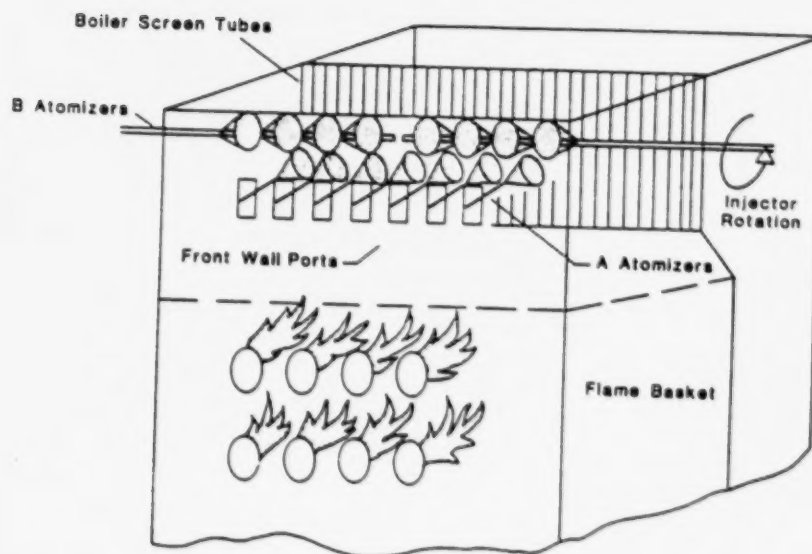


Figure 2. Schematic of A and B Atomizers Position

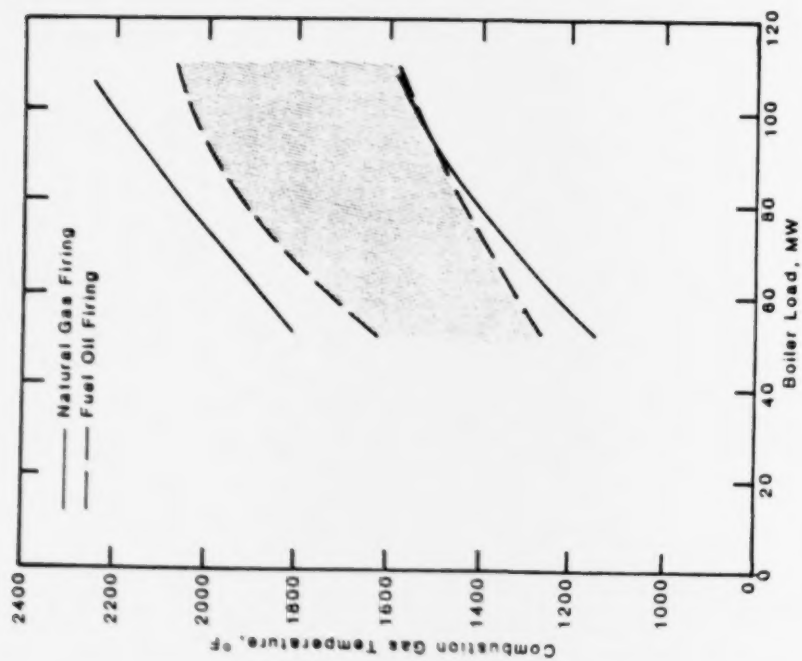


Figure 3. Combustion Gas Temperature Versus Load - Natural Gas and Fuel Oil Firing

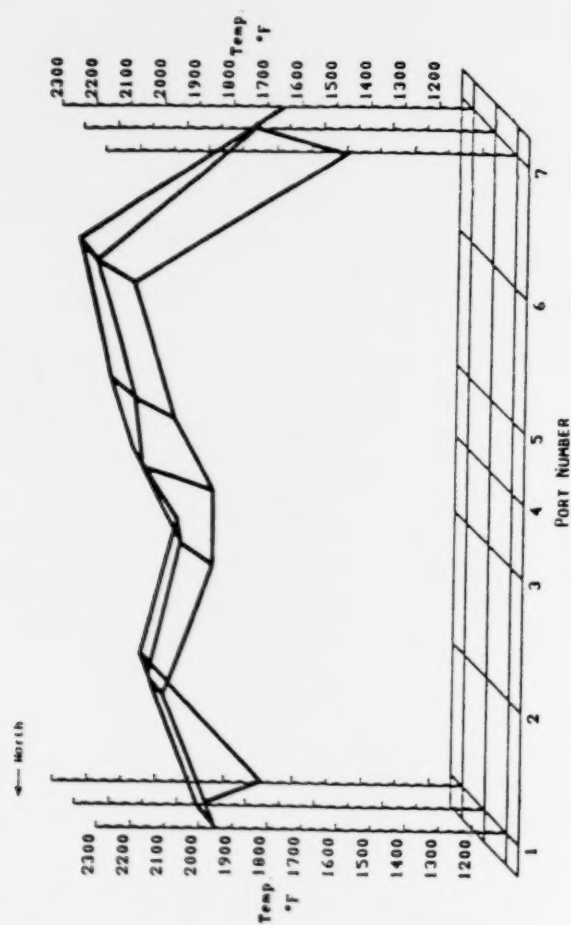


Figure 4. Combustion Gas Temperature Profile at Furnace Exit, 110 MW, ABIS, Natural Gas

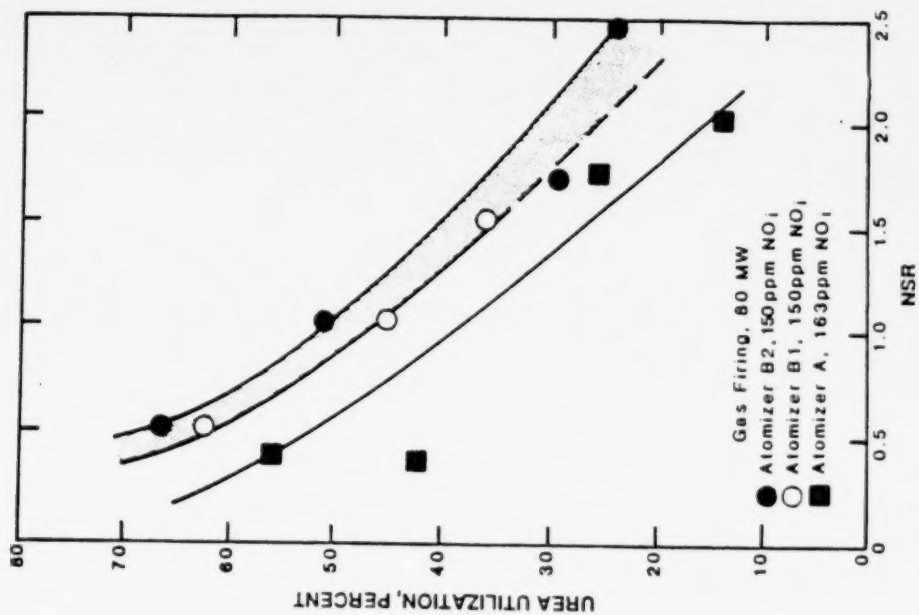


Figure 6. Effect of Injection Parameters on Urea Utilization

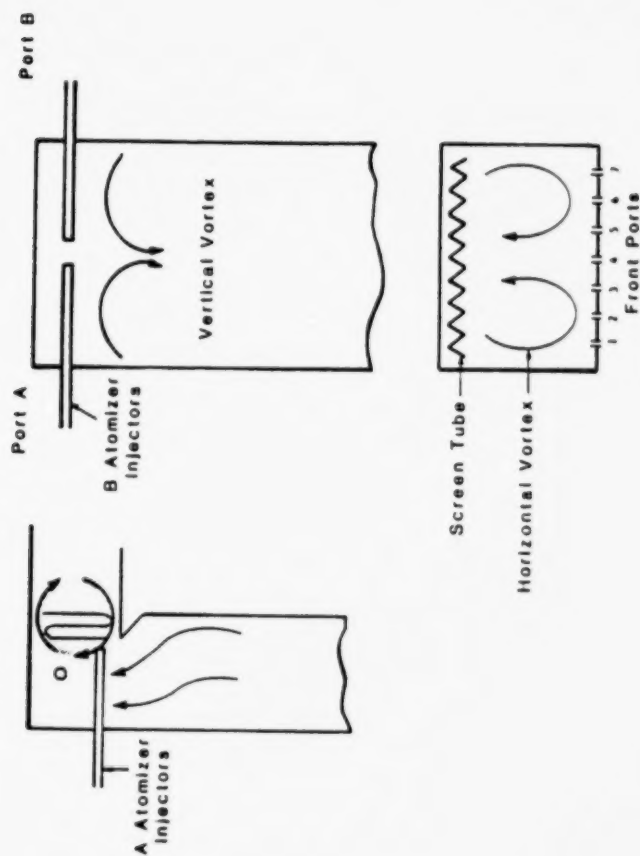


Figure 5. Schematic of Furnace Recirculation Zones

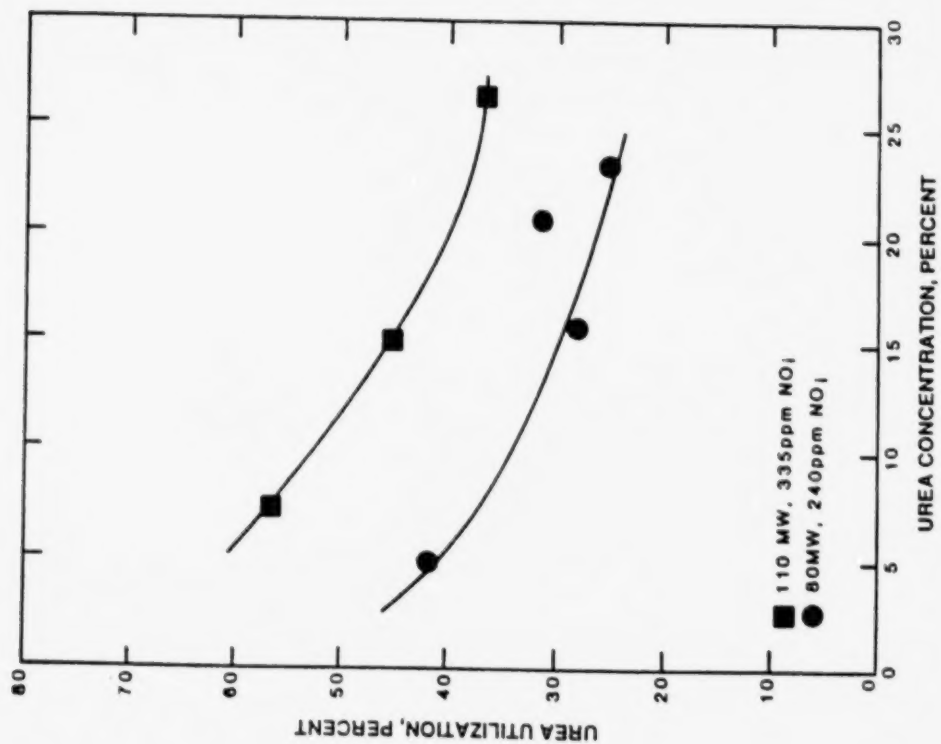


Figure 7. Effect of Urea Concentration on Utilization

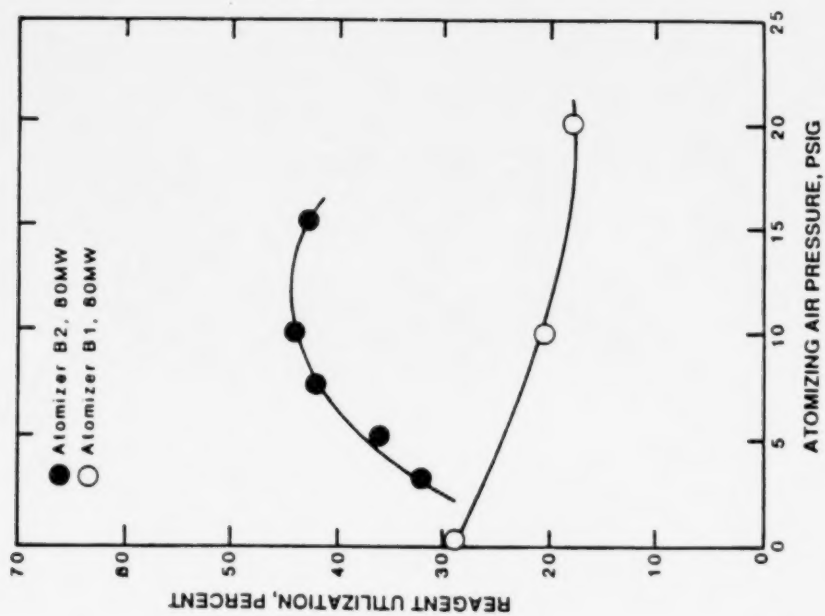


Figure 8. Effect of Atomization Pressure on Utilization

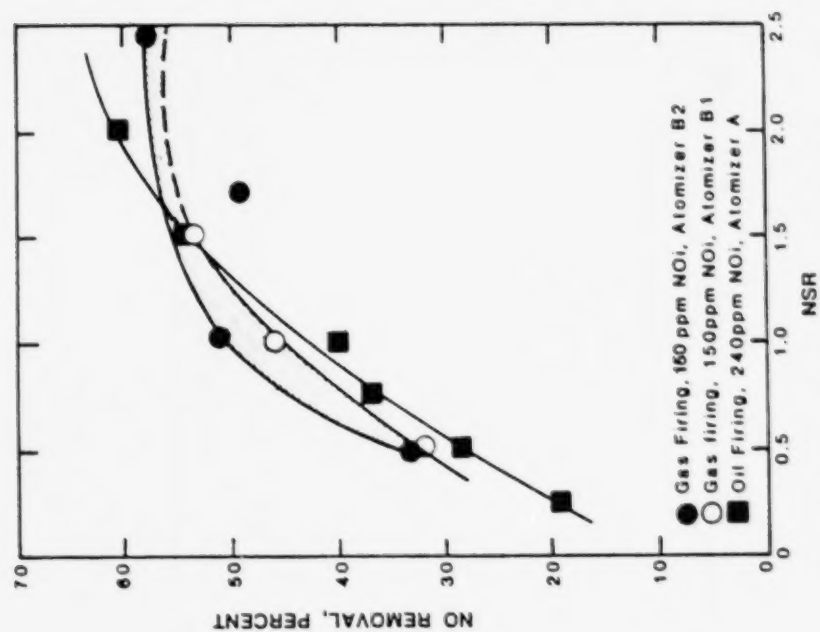


Figure 9. NO Removal as a Function of NSR - 80 MW

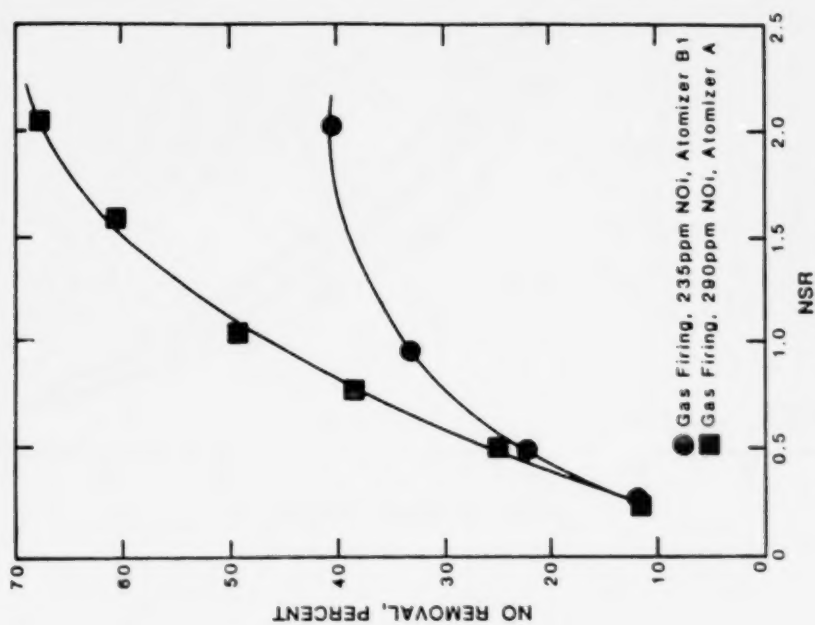


Figure 10. NO Removal as a Function of NSR - 110 MW

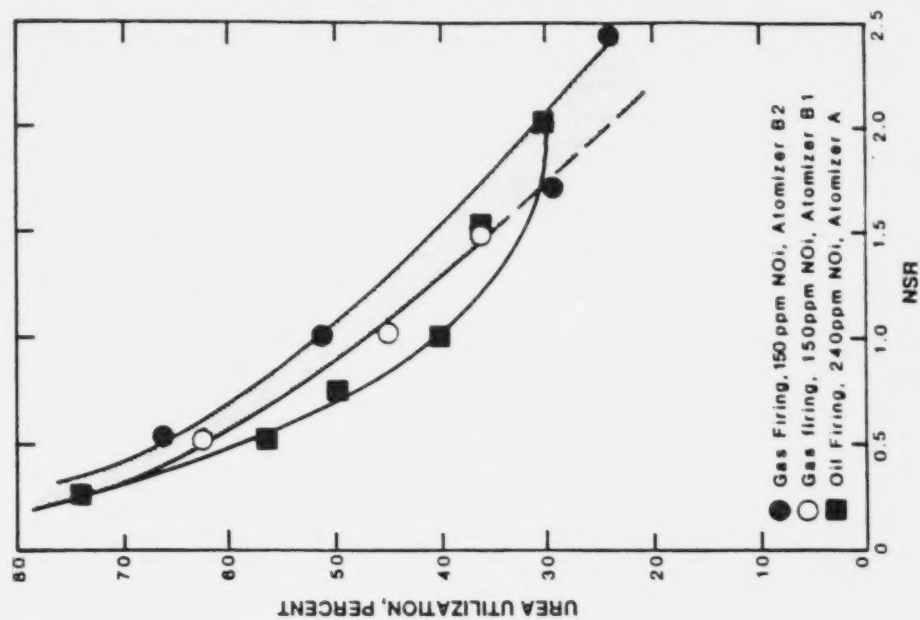


Figure 12. Change in Urea Utilization with NSR - 80 MW

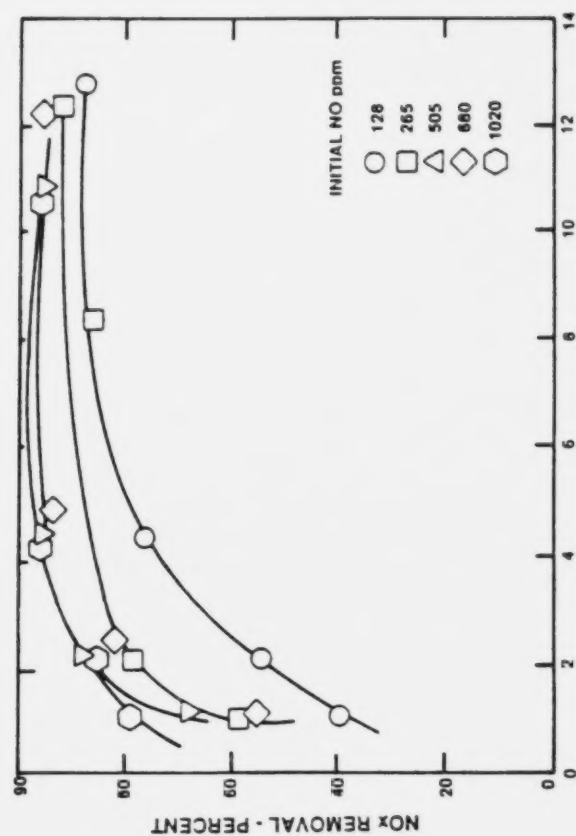


Figure 11. Effect of Initial NO Concentration on NO Removal - Laboratory Data

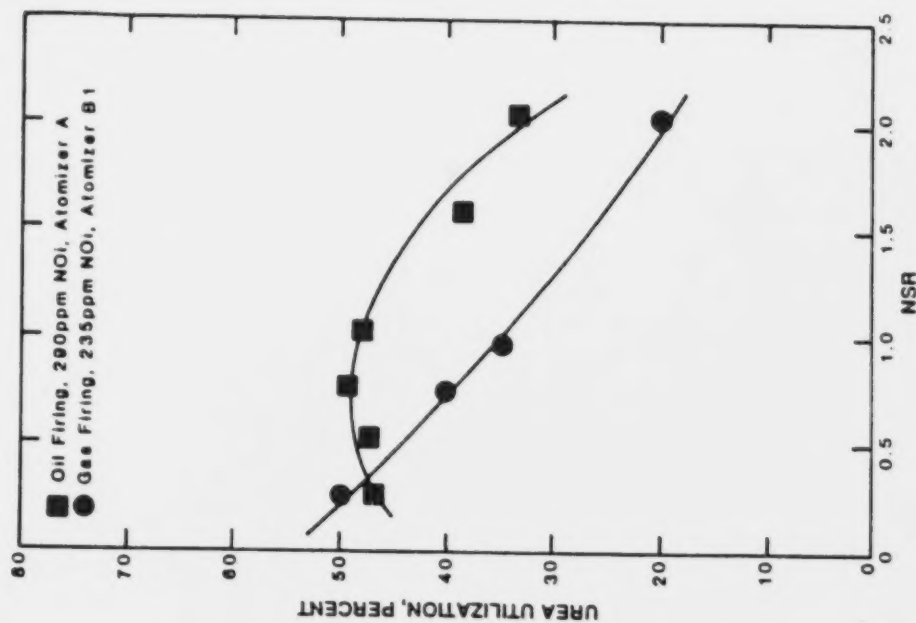


Figure 13., Change in Utilization with NSR - 110 MW Load

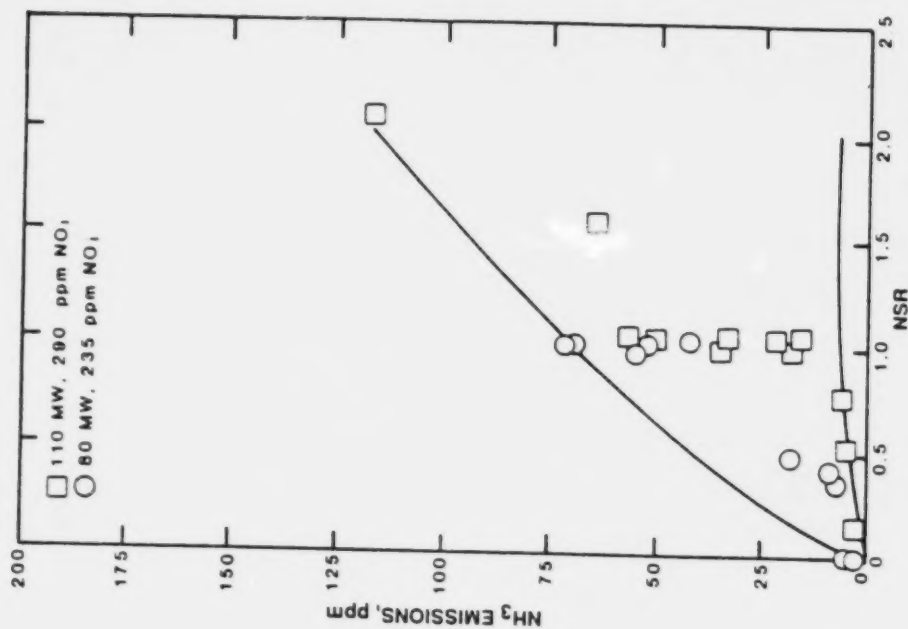


Figure 14. NH₃ Emissions Resulting from Urea Injection During Fuel Oil Firing

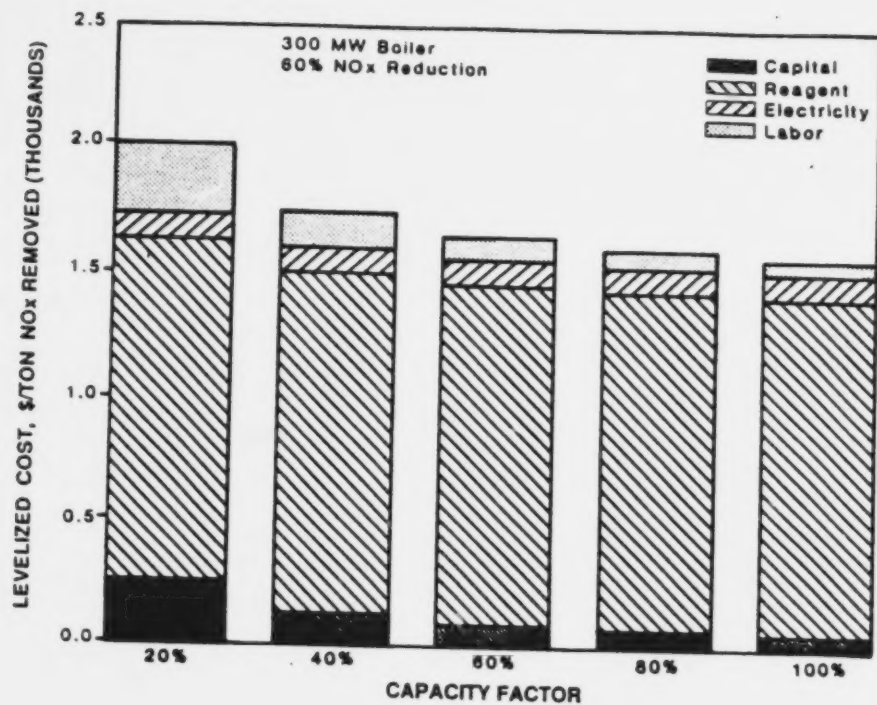


Figure 15. Levelized Cost of Emissions Reduction

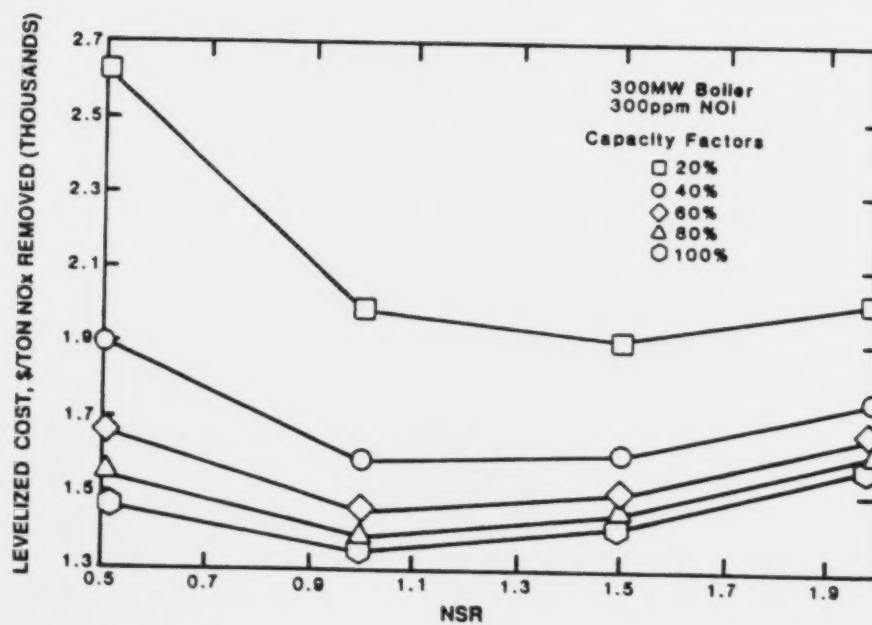


Figure 16. Sensitivity of the Cost of the Technology to NSR

TABLE 1. UREA PROPERTIES

	Prilled	Granular	Aqueous Solution
Chemical Formula	(NH ₂) ₂ CO	(NH ₂) ₂ CO	(NH ₂) ₂ CO
Bulk Density, lbs/ft ³	49	48	
Melting Point, °F	270.8	270.8	
Specific Gravity @ 60°F			1.14
Pounds per Gallon @ 60°F			9.5
Crystallization Temperature			64°F
Corrosivity			Non-Corrosive
General			
Shipping Containers	Bag (80 lbs) - truck or rail Bulk - tarped hopper trucks, covered rail hopper cars, or boxcars	Clean, covered hopper trucks	Bulk tank trucks

TABLE 2. SUMMARY OF PARAMETERS USED TO PERFORM THE ECONOMIC EVALUATION

FINANCIAL FACTORS Type of Security	% of Total	Current Dollars		Constant Dollars	
		Cost	Return	Cost	Return
Debt	50	11.0%	5.5%	2.3%	1.1%
Preferred Stock	15	11.5%	1.7%	2.8%	0.4%
Common Stock	35	15.3%	5.3%	6.3%	2.2%
Total Annual Return (Discount Rate)			12.5%		3.7%
Inflation Rate			8.5%		
Federal and State Income Tax Rate			50.0%		
Investment Tax Credit			10.0%		
TAX AND BOOK LIFE (1)					
Plant Class (2)		Tax Recovery (3)		Book Life	
Fossil-Fueled Generation					
Transmission & Distribution		15 years		30 years	

- (1) See Section B-2.4.3 of TAG analysis for details
 (2) Electric utility tax accountants generally agree that, until appropriate tax rules are promulgated, a 10-year tax life should be used for emerging technologies involving renewable sources.
 (3) Based on the federal tax laws in effect on December 31, 1981

TABLE 3. CAPITAL COST FOR UREA INJECTION SYSTEM

Plant Capacity MW	Total Capital Cost \$1,000	Capital Cost \$/kW of Generation
100	667	6.7
300	761	2.5
500	846	1.7

RETROFIT COMBUSTION CONTROLS FOR GAS/OIL-FIRED UTILITY BOILERS

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INTRODUCTION

The NO_x Reduction Program, a voluntary undertaking by the City of Los Angeles, Department of Water and Power (LADWP), was initiated after assessing that utility boilers in the Los Angeles Basin are becoming targets for additional NO_x controls and that Rule 1135.1 NO_x settlement limits may be exceeded in the future under certain dispatch and fuel use scenarios. The program is based on two objectives:

1. To implement measures that will assure continued compliance with the Rule 1135.1 NO_x settlement emission limits, which could be exceeded sometime in the 1990's under certain resource scenarios such as unavailability of natural gas or hydroelectric import energy.
2. To evaluate advanced low-NO_x combustion technology capabilities systems as an alternative to postcombustion treatment for retrofit on existing low capacity factor utility boilers. Combustion controls appear to be significantly more cost effective than postcombustion treatment, and their installation could be incorporated with other compatible boiler modifications that would improve boiler reliability and thermal performance.

The LADWP NOx Reduction Program is designed to accomplish these overall objectives through a three-phase approach. Phase 1 was an engineering evaluation of advanced combustion NOx control techniques applicable to LADWP oil/gas-fired boilers; Phase 2 involves the design, fabrication and installation of a low-NOx demonstration system on one LADWP boiler; and Phase 3 will be the test, evaluation, and demonstration of the installed low-NOx technology.

Specific tasks performed to accomplish the Phase 1 objective were: (1) to identify and screen applicable NOx control alternatives; (2) to assess commercial experience with advanced low-NOx combustion technology in Japan; (3) to solicit preliminary technical/budgetary proposals from Babcock and Wilcox (B&W) and Combustion Engineering (C-E) which provide estimates of NOx emissions control capabilities specifically for the LADWP units; (4) to analyze the information from Japanese installations and the boiler manufacturers proposals; and (5) to select a boiler and NOx control technology for consideration in Phase 2.

The work was performed jointly by LADWP and its consultants, Electric Power Technologies (EPT) and Electric Power Services International. This paper summarizes the results of Phase 1 activities and plans for Phases 2 and 3.

TECHNOLOGY DESCRIPTIONS

A variety of advanced combustion control technologies for NOx emissions have evolved during recent years, particularly in Japan. These technologies are briefly described below.

Low-NOx Burners with Overfire Air and Flue Gas Recirculation (LNB's)

This advanced combustion control technology has been widely applied on a commercial basis in Japanese power plants. All major Japanese utility boiler manufacturers commercially offer LNB's. While the details differ significantly among manufacturers, all low-NOx burners operate on the same basic principles. By one means or another, they all modify the air and fuel introduction processes which slow the rate of mixing, reduce oxygen availability in critical NOx formation zones, and reduce peak flame temperatures. It is important to note that overfire air (i.e., two-stage combustion) and flue gas recirculation are almost always incorporated into the design of these burners. Two-stage combustion and flue gas recirculation has extensively been used in the U.S. for control of NOx emissions on oil and gas-fired boilers. The combination of these techniques with LNB's has been integral to the success of LNB's in Japan.

B&W offers the "PG-DRB" (i.e., Primary Gas - Dual Register Burner) burner under a licensing agreement from Babcock-Hitachi (BHK). The PG-DRB burner, illustrated in Figure 1, is different from the B&W dual register burner licensed to BHK several years ago in several ways, including: (1) The aerodynamics have been optimized (i.e., throat and annular dimensions, air distribution, swirl and register design) for gas mixing and flame stability; (2) Pure recirculated flue gas is introduced through an annular sleeve between the primary and secondary air exits; (3) the natural gas distributor system is specially designed for creating low-NO_x formation combustion zones; and (4) the oil atomization spray tip is asymmetrically designed for stratified fuel injection.

C-E similarly offers "ROPM" wall-mounted burners for oil and gas-fired boilers under a licensing agreement from Mitsubishi Heavy Industries (MHI). Figures 2 and 3 illustrate the ROPM burners for oil and gas-firing respectively. To date, MHI has not installed a combination burner that can fire oil and gas, however, one has been designed and is being offered through C-E for the LADWP boilers.

Reburning

Reburning is a relatively new combustion NO_x control technology. The technology is known by various trade names depending on the manufacturer. The C-E system (licensed from MHI) is known as "MACT" (i.e., Mitsubishi Advanced Combustion Technology) while the B&W system (licensed from BHK) is referred to as in-furnace-NO_x-reduction, or "IFNR".

Table 1. DESCRIPTION OF REBURNING PROCESSES

NAME	APPLICATION	ESTIMATED NO _x REDUCTION	TERMINOLOGY
Full Reburning (or Reburning)	Large Furnaces (coal capable)	50% (all loads)	B&W - "IFNR" C-E - "MACT"
Partial Reburning	Oil/Gas Capable Furnaces	20-30% at full load, 50% below 75% load	B&W - Pseudo IFNR C-E - Partial MACT
Dual-Mode Reburning	Oil/Gas Capable Furnaces	50% below 70% load	B&W - Dual-Mode IFNR

Regardless of the name, reburning works on the same basic principle: the oxygen atom in NO can be extracted by creating a fuel rich, chemically reducing environment at the correct temperature. The remaining nitrogen atom ultimately is converted to harmless molecular nitrogen (N₂).

Reburning processes can be further categorized as shown in Table 1. It should be noted that the terminology shown is not universally utilized.

Flue Gas Recirculation (FGR) with Existing Burners

This straight-forward technology application involves recirculation of flue gas to the windbox to combine with combustion air. For LADWP boilers, this technique would be integrated with the the current mode of low-NO_x operation (i.e., burners-out-of-service or BOOS).

Conversion of Face-fired Units to Tangential Firing

C-E and MHI manufacture new boilers that are tangentially fired with burners located in the furnace corners. Tangential firing characteristically provides for extended combustion (delayed mixing of the fuel and air) and somewhat lower NO_x than opposed-fired boilers with wall-mounted burners. In one instance in Japan, MHI converted a wall-fired boiler to tangential-firing which resulted in NO_x reductions.

STUDY MISSION TO JAPANESE UTILITIES AND BOILER MANUFACTURERS

During Phase 1, a delegation of LADWP engineers and consultants toured Japanese facilities for fourteen days to assess the NO_x levels achieved in commercial retrofit situations similar to those at LADWP. Japan is the only location in the world with a significant number of boilers which have been retrofit with advanced NO_x control technologies. In addition, a key objective of the tour of Japanese power companies and manufacturers was to assess other factors critical to a successful commercial application of NO_x controls, including by-product emissions and operating and maintenance experience for retrofit installations. The following organizations were visited in Japan: Tokyo Electric Power Company; Joban Joint Power Company; Chugoku Electric Power Company; Electric Power Development Company; Chubu Electric Power Company; Babcock Hitachi; and Mitsubishi Heavy Industries.

Each of the companies visited provided significant information closely related to the LADWP circumstances. The Tokyo Electric Power Company (TEPCO) has more experience with advanced combustion NO_x controls on oil and gas-fired boilers

than any other utility in the world, and hosted the LADWP delegation for half of the tour.

Observations and Findings

In general, the tour of Japanese facilities provided considerable confidence for LADWP to move forward with installation of an advanced combustion NOx control system. However, accompanying technical issues were identified which strongly supports the LADWP approach to pursue a demonstration prior to committing to widespread commercial application.

Key findings from the tour of Japanese advanced combustion NOx control technologies are listed below.

Low-NOx Burners

1. There are dozens of successful commercial retrofit installations with many having 10 years operating experience.
2. Typical NOx levels are 50-60 ppm (@ 3% O₂) on natural gas and 90-130 ppm (@3% O₂) on oil fuel. Actual NOx levels on any particular boiler are, of course, highly dependent on the specific details of the boiler design.
3. Boiler manufacturers (BHK and MHI) have equivalent NOx control capabilities.
4. Low-NOx burners require overfire air, flue gas recirculation, and advanced control systems to realize the NOx levels achieved in Japan.
5. Pressure part changes, which can be expensive, have not been required when retrofitting low-NOx burners.
6. Low-NOx burners have had no adverse impact on operations and maintenance, including: full load capacity, thermal efficiency, forced outages, tube failures, or personnel requirements. However, Japanese operating and maintenance practices are significantly different from typical U.S. practices.

Reburning

1. Reburning is a relatively new technology, but several units now have as much as 5 years commercial experience .
2. All reburning experience to date is on large, coal-capable furnaces.
3. No partial or dual mode reburning installations were observed in Japan, however, manufacturers claim these systems are technically feasible.
4. Achievable NOx levels with any form of reburning are highly boiler specific and require detailed analysis by the manufacturer.
5. Pressure part changes are frequently required to successfully apply reburning.

Unresolved Technical Issues

While the Japanese low-NOx burner and reburning experience to date has been successful, critical examination of the Japanese experience reveals several major unresolved technical issues when applied to the LADWP situation. These unresolved technical issues translate into a direct measure of the risk involved in applying these technologies. Table 2 summarizes these unresolved issues.

PRELIMINARY TECHNICAL/BUDGETARY PROPOSALS FROM B&W AND C-E

LADWP solicited preliminary proposals from B&W and C-E for each of the units at Haynes and Scattergood Generating Stations. Both manufacturers were encouraged to provide comparative bids for all of the units regardless of the original vendor. They were instructed that LADWP is interested in state-of-the-art technology that would produce minimum NOx emissions for the units under consideration. The manufacturers submitted cursory bids in Fall 1985. As a result of a series of meetings in Los Angeles and Japan, the bids were revised several times. The final bids were received in June 1986.

B&W submitted bids for Haynes 3&4 and Haynes 5&6 only. They declined to bid on Scattergood 3 because it was a tangentially-fired boiler and they offer no compatible technology. B&W also declined to bid on Haynes 1&2 and Scattergood 1&2 because they were not the original equipment manufacturer (OEM) and also questioned the compatibility of their technology. (B&W may submit bids for these units if they were selected for Phase 2). C-E bid all of the units.

Table 2. UNRESOLVED TECHNICAL ISSUES FOR LOW-NO_x BURNERS AND REBURNING

UNRESOLVED ISSUE	POTENTIAL PROBLEM	COMMENTS
o Particulate Matter Emissions and Opacity	- o Significant potential for increased particulates on oil-firing low-NO_x burner. - o Higher risk potential for reburning with oil-firing.	- o Particulates include mass and PM₁₀. - o Japanese use an ESP to control particulates on oil firing. - o Increased excess air is recommended measure. - o Not a concern for gas. - o Increased excess air for carbon burnout will also increase NO_x levels.
o NO_x Emissions at loads below 30%	o NFPA safety requirements may increase NO_x levels dramatically due to high excess air levels.	- o Japanese have no experience below 30% load. - o Current LADWP boilers are not operated often below 30% load due to boiler limitations. - o LADWP examining boiler modifications to permit operation to 10% load.
o Partial and Dual-Mode Reburning not Commercially Proven.	- o NO_x levels and particulate matter emissions achievable cannot be accurately predicted. - o Unpredictable operations and maintenance problems.	- o Since no commercial experience, difficult to anticipate problems - o Manufacturers are confident in success. - o Reburning can be off boiler will operate normally.

TABLE 2. UNRESOLVED TECHNICAL ISSUES FOR LOW-NOx BURNERS AND REBURNING

UNRESOLVED ISSUE	POTENTIAL PROBLEM	COMMENTS
o Co-firing Gas/Oil fuel on wall-fired boilers	o NOx levels may increase for NOx burners and reburning when co-firing.	o No Japanese experience. o Achievable NOx levels during co-firing may depend on burner control system capabilities.
o Reburning not proven for co-firing.	o High NOx and carbon particulate levels. o Flame instability.	o No Japanese experience. o Problems which could be encountered are difficult to establish.
o CE/MHI Gas-and-Oil Low-NOx Burner for Wall-fired Boiler.	o No previous experience.	o MHI/CE are confident in their design capability. o Burner would be built and tested first in Japan.
o CE/MHI Wall-Fired Reburning	o No previous experience.	o MACT T-fired experience would be basis, but new development required.
o Required O&M Practices Greater than that Common to LADWP	o Decreased reliability. o NOx and particulate levels increase over time.	o Dedicated O&M manpower necessary to realize anticipated NOx levels.

Low-NOx burners (with overfire air and flue gas recirculation) were bid for all units except Haynes 5&6. Partial reburning was bid for Haynes 5&6 by both B&W and C-E. In addition, C-E estimated the cost for converting to tangential-firing Haynes 1&2 and Haynes 5&6. The associated NOx reduction benefit was estimated by C-E to be an additional 10% as compared to wall-firing low-NOx combustion. Because of the extra cost, marginal NOx benefit, and inherent technical risk, conversion to tangential-firing was discounted in the selection process.

Target NOx reductions for gas-firing ranged from 46 to 83% for the wall-fired boilers, and was only 17% for Scattergood 3, the only tangentially-fired boiler. For oil-firing, the target NOx reductions ranged from 46% to 72%. The "target" level represents a 90% confidence on behalf of B&W and C-E. B&W and C-E also provided estimates of the lowest NOx levels that might be achieved: 25 to 59 ppm for gas, and 60 to 113 for oil. These levels are comparable to those observed in Japan for similar fuels. "Guaranteed" NOx levels can be expected to be marginally higher than those for the 90% confidence level.

As an aside, an interesting observation can be made regarding the capital cost figures bid by B&W and C-E for retrofitting low-NOx burners. Their preliminary cost quotations are significantly higher than estimates provided informally by U.S. manufacturers in the past, which have typically been in the \$5-10/kW range. Furthermore, inclusion of required modifications that are not included in the bids and other indirect expenses may more than double the capital cost. Reasons for these differences are not obvious. The proposed demonstration project will provide a basis for estimating the cost of other advanced combustion NOx control retrofits.

SELECTION CRITERIA

Fourteen criteria were identified which served as the basis for the boiler/technology evaluations.

1. NOx REDUCTION POTENTIAL AT FULL LOAD. NOx emissions are typically highest at full load on both concentration (i.e., ppm) and emissions rate (i.e., lbs/hr) bases. Hence, full load is typically the "design point" for a specification and the operating condition for bid comparisons. Emission guarantees would be specified at full load.
2. NOx REDUCTION AT LOW LOADS. The Haynes and Scattergood units are forecast to have low capacity factors for the next several years and will operate a significant amount of the time at lower loads, including minimum load. The NOx emission at rates these lower loads will be a major contributor to the total mass emissions on an annual basis.

3. APPLICABILITY OF THE RESULTS TO OTHER LADWP BOILERS. The results from the demonstration unit will serve as a basis for evaluating low-NOx technology to other boilers in the LADWP system, and will provide a design basis for more accurate predictions of cost and guaranteed NOx levels. Therefore, it is important that the selected demonstration unit be representative of the other boiler designs in terms of size, heat release rate, and firing configuration.
4. INNOVATIVENESS OF SELECTED NOx TECHNOLOGY. The demonstration project will attempt to demonstrate "leading-edge" or best available technology that provides for the greatest NOx reduction using combustion technology.
5. PROBABILITY OF SUCCESS. The demonstration project will likely constitute a first-time application of the NOx technology in the United States. Some of the proposed technologies would require new designs and represent first-time applications anywhere in the world. There is also the possibility that the selected manufacturer may not be the supplier of the original equipment. These factors and others have to be considered when assessing the technical and financial risk (probability of success) for the project.
6. SIMILAR EXPERIENCE IN JAPAN. Where there has been similar experience in Japan, the NOx reduction predictions, cost estimates, and probability of success estimates are more reliable. In addition, assistance from Japanese utilities may be more readily available with respect to O&M practices.
7. VENDOR QUALIFICATIONS/JAPANESE SUPPORT. The technologies of interest are licensed by B&W and C-E from their Japanese counterparts who have significantly more experience. The Japanese "know-how" must be transferred to B&W and C-E for the project to be successful. In addition, if it is a first-time application in the U.S., direct involvement of the Japanese manufacturer is desirable.
8. CAPITAL COST. The absolute cost of the technology for the demonstration project could be a determining factor for selection if technical comparison are relatively equivalent.
9. COST EFFECTIVENESS. Similar to Criterion 9, the normalized costs on a \$/kW basis could be a determining factor.
10. IMPACT ON BOILER O&M AND RELIABILITY. The installation of a low-NOx combustion system will constitute a major modification to the boiler. Depending upon the complexity of the system, its firing characteristics, and heat flux patterns (as compared to the system it is replacing) the O&M requirements and boiler reliability could be impacted (good or bad).

11. NOx TONNAGE REDUCTION FOR DEMONSTRATION UNIT. The project should demonstrate an appreciable NOx reduction on a mass emissions basis. Therefore, the preferred demonstration unit should be characterized by high baseline NOx levels, appreciable NOx reduction potential, oil-firing capability, higher capacity factors, and larger unit sizes.
12. IMPACT ON PARTICULATE MATTER EMISSIONS AND OPACITY. Increased particulate matter emissions levels are not acceptable. The low-NOx combustion technologies may or may not (relative to current BOOS operation) produce more particulate matter emissions. Since the Japanese experience is not clear on this subject, critical evaluation of technology alternatives with respect to the controllability of combustion generated particulates is imperative.
13. COMPATIBILITY WITH OTHER MAJOR MAINTENANCE PROJECTS. The installation of the low-NOx combustion technology will require a major unit outage and constitute significant modifications to the boiler. The consequential effects of the NOx Reduction Project on other planned projects (and vice versa) must be considered. It could result in significant cost savings if major projects could be optimally coordinated.
14. OTHER SCREENING CRITERIA. In addition to these selection criteria, LADWP imposed screening criteria as follows. NOx reduction techniques are eliminated from consideration if: (a) currently being applied by LADWP; (b) previously tested by LADWP and been shown to be unsatisfactory; (c) boiler efficiency penalties of over 1 percent are produced; (d) NOx reductions of greater than 30% are not achieved; or (e) the technique is not considered innovative nor useful for advancing NOx control in the United States.

BOILER/TECHNOLOGY EVALUATIONS

Each of the Haynes and Scattergood units and the proposed NOx technology options were evaluated for selection. The evaluation process relied heavily on engineering judgement. A discussion of factors considered to be important is discussed below for each potential demonstration case.

Scattergood 1&2 with Low-NOx Burners

The Scattergood 1&2 boilers are single-wall fired and were manufactured by C-E. They are the smallest boilers and have the lowest heat release rate among those being considered for the project. C-E proposed retrofitting a wall-fired ROPM burner to achieve NOx reductions of 57% and 50% for gas and oil-firing.

respectively, which represents a significant NOx reduction at full load. However, since the units are the smallest and the capacity factors are relatively low, the demonstrated NOx reduction (mass basis) would be much less than for other units. Results from a demonstration on Scattergood 1 or 2 would be directly transferable to the Haynes 1&2 units. Some extrapolation would be required for the other Haynes units because they have higher heat release rates, are opposed-fired, and Haynes 5&6 are slightly larger. The dual-fuel ROPM burners would be a first-time application for C-E or MHI and presents a limited technical and economic risk for the project. B&W did not submit a proposal for these units.

Scattergood 3 with Low-NOx Burners

Scattergood 3 is unique among the boilers being considered because it is the largest, is tangentially-fired, has the highest heat release rate, fires only gas fuel, operates on a derated basis, and baseline NOx emissions (concentration basis) are approximately one-fourth of that for the other units. Hence, demonstration on Scattergood 3 should only be considered as a design basis for converting other boilers to tangential-firing.

Only C-E submitted a bid for Scattergood 3 which was for the "PM" low-NOx burner system. Reburning cannot be considered because the furnace is too small (per unit heat input). NOx reductions for gas-firing of only 17% are predicted. This is due, in part, to C-E's lack of familiarity with the accomplishments by LADWP with the existing system to reduce NOx. It will likely be possible through fine-tuning to achieve NOx levels below the 25 ppm level predicted by C-E. These predictions are all for 380 MW and it was not clear whether reduced NOx capability would result in higher load operation or reduced NOx emissions (mass basis).

There is corresponding experience in Japan for this technology application, the proposed cost are reasonable, and the risk to operations appears minimal, hence, the probability of success for a demonstration project at Scattergood 3 would be very high. However, the unit is not the Consultant's recommendation because it would be unique and the results would not have system-wide application unless LADWP seriously were considering conversion of the other boilers to tangential-firing.

Haynes 1&2 with Low-NOx Burners

These units have boilers very similar to Scattergood 1&2. Accordingly, all four units were judged to have very similar strengths and weaknesses for the demonstration project. However, Haynes 1&2 does have a few features that make it slightly more attractive. The boilers are larger and have approximately the same furnace size as Haynes 3&4 and heat-release rate as Haynes 3-6, hence, extrapolation of the results to the other units will be more straightforward. The cost for the project on a (\$/kW) basis would be about 35% less for Haynes 1&2 as compared to Scattergood 1&2. The major unknown at each site is how

closely the NOx Reduction Project would dovetail with other major maintenance or upgrade work planned for the units. For example, Haynes 1 has recently finished a major outage for tube replacement and a similar outage is needed for Haynes 2. Notwithstanding this latter consideration, Haynes 1&2 would be recommended over Scattergood 1&2 on the basis of boiler size and cost effectiveness.

C-E also submitted information for converting Haynes 1 or 2 to tangential-firing. The additional NOx reduction was predicted to be 10 to 15% depending upon the fuel and firing condition. There is a fairly high technical, and therefore financial, risk associated with such a major modification. Based on these preliminary cost and performance estimates this option is not recommended for Phase 2 consideration.

Haynes 3&4

The boilers on Haynes 3&4 were manufactured by B&W and have many important features which are similar to the other units (excepting Scattergood 3). The units are 230 MW each which is the same as Haynes 1&2 and midway between Haynes 5&6 and Scattergood 1&2. Similarly, the heat release rate is at the middle of the range for the LADWP boilers.

B&W submitted two bids: low-NOx burners and dual-mode reburning. C-E submitted one bid for partial reburning. All three bids are discussed below.

B&W Low-NOx Burners. This proposal has many attractive features including: significant NOx reduction (66% for gas and 58% for oil); the results would be directly applicable to the other boilers; the control technology would be a first-time application in the United States but there is a large base of experience in Japan for similar boilers; it is the lowest cost bid; impact on O&M would be minimal; and it is judged to have the highest probability of success among all the units (equivalent to that for Scattergood 3). The only significant concern would be the potential impact on particulate matter emissions for oil-firing, but this is a similar concern for all the cases. Due to the recognized technical merits of this technology, the low risk, and minimum cost, this was the top recommendation for Phase 2 consideration.

B&W Dual-Mode Reburning. For this configuration, the boiler and combustion system would be almost identical to that described above for Low-NOx burners between 70% and full load. At 70% load and below, additional burners would be employed to create reburning and additional NOx reduction. In fact, the NOx reduction estimates of 83% for gas firing and 72% for oil-firing are comparable to that for SCR technology applied to the current BOOS operation. The dual-mode system is clearly the most innovative among the proposal received from B&W and C-E. It is unproven, however, and therefore presents some risk. Overall, the risk is limited because if the reburning mode does not work, the low-NOx burner mode may still be invoked over the load range. The added cost for this increased flexibility is substantial.

C-E Partial Reburning. Dual-fuel ROPM burners (first-ever by C-E or MHI) would be installed in the existing burner locations and additional burners and overfire air ports would be added to complete the MACT partial reburning system. C-E predicts NOx reductions of 70% for gas and 65% for oil for this configuration at full load. Although it was not confirmed by C-E, greater NOx reductions may be expected at lower loads. There is additional technical risk because C-E/MHI have not previously applied the MACT system to a wall-fired boiler, nevertheless, good vendor support can be expected. The system would also be fairly expensive.

Haynes 5&6.

The boilers on Haynes 5&6 are unique to the LADWP system for both their firing systems (cell burners) and steam circuitry (supercritical pressure/double reheat). Due to their size and inherent thermal efficiency they operate at higher capacity factors than other LADWP units when not limited by forced outages. In recent years the number and duration of boiler outages has been unsatisfactory. Hence, the boilers have been identified for major upgrading and there is the distinct possibility that the NOx Reduction Project could be coordinated with other major boiler maintenance projects to the benefit of LADWP. Assessing the value of dovetailing major projects on Haynes 5&6 was beyond the capability of the Consultants, hence, recommendations presented here did not give this possibility high consideration.

The Haynes 5&6 boilers are the largest and have the highest heat release rates among the wall-fired boilers, and therefore, would represent the greatest degree of extrapolation of the demonstration results to the other boilers.

B&W and C-E each submitted one bid for Haynes 5&6 which used partial reburning for the NOx technology. Each of these cases is discussed below. In addition, C-E provided limited information for converting to tangential-firing with partial reburning; this is also discussed.

B&W Partial Reburning. B&W proposed "Pseudo IFNR" as the NOx reduction technique. It would require a complete rebuild of the firing walls in the furnace. The resulting NOx reduction is predicted to be 66% at full load (and possibly higher at reduced loads). It was implied by B&W that this technology is being applied to one boiler at the Chubu Electric Company in Japan. Chubu Electric did not confirm this information, hence, Haynes 5&6 must be considered as a first-time application of Pseudo IFNR. Since reburning would be invoked at all loads, the concern for increased particulate matter emissions for oil-firing is higher for this technology option than for only low-NOx burners. Due to the advantages of high NOx reduction potential, innovative technology, and cost effectiveness this option deserves high consideration for Phase 2. When directly compared to the Haynes 3&4 options, however, it is a second choice because the probability of success is lower and the absolute costs are higher.

C-E Partial Reburning. The C-E proposal was very similar to those above for B&W on Haynes 5&6 and C-E for Haynes 3&4. This option has all the technical advantages discussed above for B&W's Haynes 5&6 proposal. Unfortunately, it also has several disadvantages. A major portion of the lower furnace would have to be rebuilt. It would represent first-time attempts by C-E/MHI for dual-fuel ROPM burners and MACT applied to wall-fired units. In addition, these boilers may be considered to be the most temperamental because of their steam circuitry and controls, hence, since C-E is not the original boiler manufacturer, significant additional risks must be expected due to their unfamiliarity with the design. Nonetheless, if Haynes 5&6 were selected for Phase 2 because of the B&W option (or the benefits associated with dovetailing major projects), this case should be carried forward for thorough analysis.

C-E Conversion to Tangential-Firing with Partial Reburning. One of the most innovative proposals received was to convert Haynes 5&6 to tangential-firing with "PM" burners and partial MACT. The NO_x reduction was predicted to be less than 10% better than for the C-E Partial Reburning case with ROPM burners discussed above. As discussed previously, based on these preliminary cost/performance estimates and the inherent technical risks, this option is not recommended for Phase 2 consideration.

SELECTION OF THE DEMONSTRATION UNIT

Based on assessments of the technological risks, costs, and compatibility with other projects to upgrade boiler operations, low-NO_x burners (with overfire air and FGR) was selected for demonstration. The selection of the demonstration unit was based on the following criteria:

1. Representative Application of Low-NO_x Burners. There should be confidence that the performance of the LNB's on the other units could be predicted from the test results of the demonstration unit.
2. Specific Advantages. The demonstration unit should offer more specific advantages than other units. Examples are: lower installed cost, higher percentage NO_x reduction, and possible reduction in existing boiler problems (e.g., low steam temperatures, high tube metal temperatures, etc.)
3. Specific Consideration. Various other criteria were considered including the time and length of the outage for installation, compatibility with existing LADWP planned outage schedules, and difficulty of site-specific boiler modifications.

Haynes 3 or 4 was selected for demonstration of the low-NOx burner system for the following reasons: representative size, representative heat release rate, current steam temperature deficiencies may be eliminated, most cost-effective choice, and compatibility with the low-NOx technology based on Japanese experience with similarly designed boilers.

Schedule for Low-NOx Burner Demonstration

The current schedule for the proposed demonstration on Haynes 3 or 4 is as follows:

Commence Engineering	February 1987
Start Construction	July 1989
Complete Installation/Startup	April 1990
Complete Testing	August 1990

SUMMARY

LADWP is committed to demonstration of retrofit combustion controls for reducing NOx emissions on oil and gas-fired units located in the Los Angeles Air Basin. Based on evaluations of commercially offered technologies and candidate boilers in the LADWP system, it has been concluded that oil/gas low-NOx burners in conjunction with overfire air ports and flue gas recirculation will be installed and tested on one unit. The selected unit will be Haynes 3 or 4, a 230 MW unit with a boiler manufactured by B&W. Due to the complexity of the project and the magnitude of boiler modifications involved, B&W has been tentatively selected as supplier of the retrofit equipment. Based on B&W's preliminary proposals, NOx reductions on the order of 65% for gas firing and 55% for oil firing are predicted at full load. According to the present demonstration schedule, test results could be available in 1990.

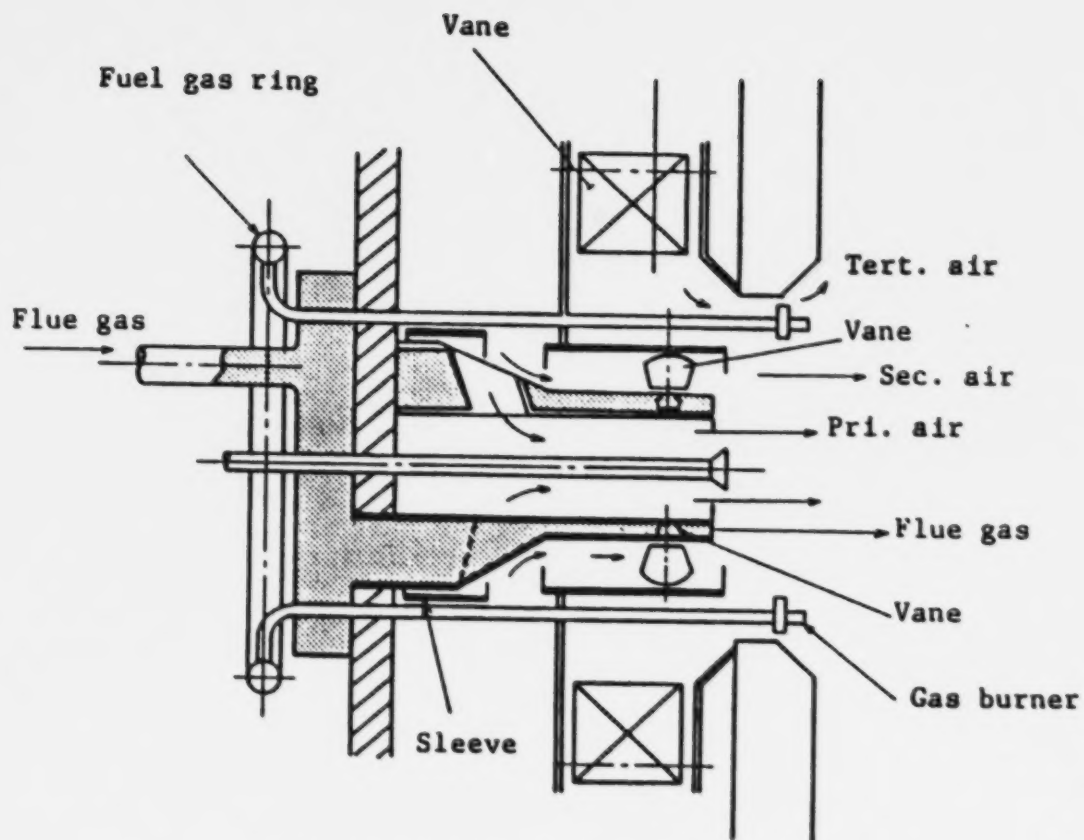


Figure 1. PG Dual Air Register Low NO_x Burner/OFA/FGR
(BHK/B&W)

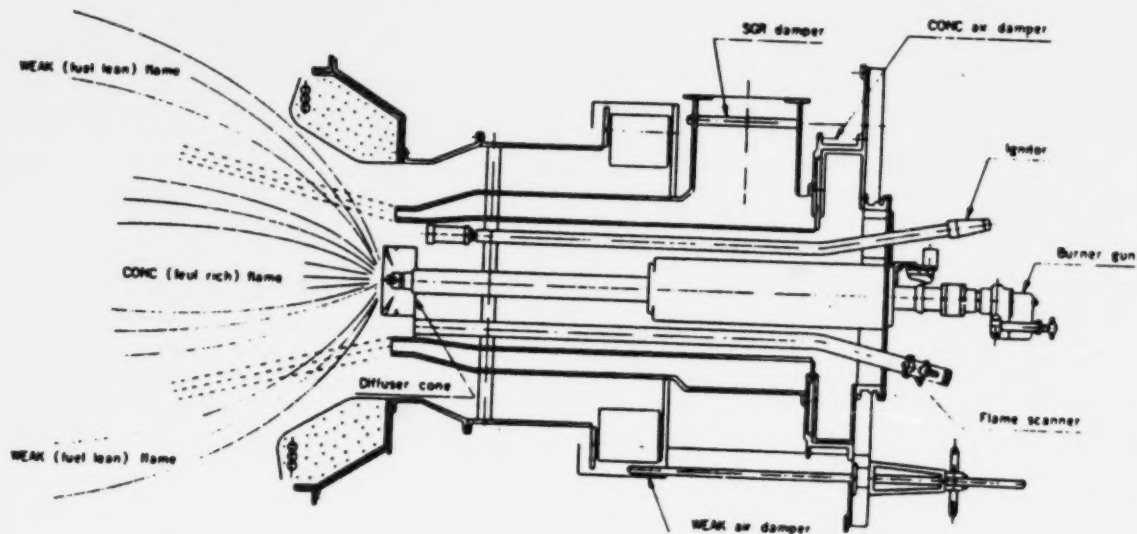


Figure 2. Structure of Oil Firing ROPM Burner

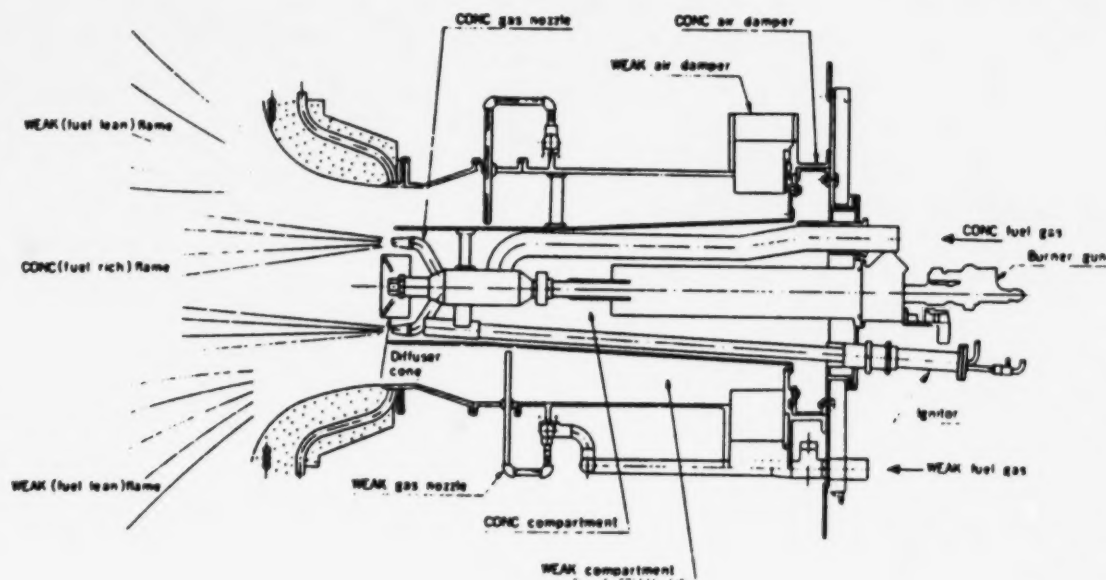


Figure 3. Structure of Gas Firing ROPM Burner

PILOT-SCALE TESTS OF A MULTISTAGED BURNER
DESIGNED FOR LOW NO_x EMISSION AND HIGH COMBUSTION EFFICIENCY

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ABSTRACT

A multistaged combustion burner design is being evaluated on a 0.6 MW package boiler simulator for in-furnace NO_x control and high combustion efficiency. An adiabatic precombustion chamber burner has been reduced in size by approximately a factor of two. Natural gas, doped with ammonia to yield a 5.8 percent fuel nitrogen content, was used to simulate a high nitrogen content fuel/waste mixture. A burner baseline NO emission of 315 ppm (measured dry, corrected to zero percent O₂) was measured, compared with an emission of over 1000 ppm estimated for a conventional, unstaged burner. Both deep air staging, resulting in a three-stage configuration, and fuel staging with undoped natural gas, yielding four stoichiometric zones, reduced the baseline NO emission by approximately 50 percent (to 160 ppm), meeting the program goal. However, deep air staging resulted in the entire front end of the boiler being fuel-rich and required penetrations into the boiler for staged air injection. Fuel staging, on the other hand, required no boiler penetrations (staged fuel and air were injected from the boiler front wall) and only a small fuel-rich flame core in the boiler (produced aerodynamically). Furthermore, sufficient air for complete oxidation of the primary combustion products was provided at the burner exit (prior to staged fuel and air injection into the boiler) in the fuel staging tests. Thus, the four-stage configuration appears to be the most promising approach for minimizing NO emissions and maximizing primary fuel/waste destruction. Further testing is ongoing with pyridine and fuel oil mixtures to better characterize surrogate fuel/waste destruction efficiency.

INTRODUCTION

The family of nitrogen oxide compounds, including nitric oxide (NO) and nitrogen dioxide (NO₂), is generally referred to as "NO_x." These NO_x are formed during the combustion of coal, oil, and natural gas by the reduction and oxidation of molecular nitrogen (N₂) and nitrogen contained in the fuel. NO₂ is a poisonous gas that the United States Environmental Protection Agency (EPA) has designated as a criteria pollutant because of its harmful human health effects [1,2]. In addition, NO_x are known to contribute to the formation of photochemical oxidants and are precursors, along with sulfur oxides (SO_x), of acid precipitation. Two more areas of concern are emerging regarding NO_x levels in the atmosphere. First, forest damage, reported to be extensive in the Federal Republic of Germany [3], has been linked with increasing

NO_x levels. Second, increasing levels of atmospheric nitrous oxide (N₂O) have been measured, levels that have been predicted to contribute to both a decline in the abundance of stratospheric ozone and an increase in climatic warming [4]. Studies of N₂O and NO concentrations in experimental flames and in flue gases have shown that a strong correlation exists between these two gases formed in combustion processes.

The EPA estimates that about 20 million tons (18 thousand Gg) of NO_x are emitted annually from stationary and mobile sources in the United States. Unlike SO_x emissions, NO_x emissions have been increasing [5]. Coal- and oil-fired utility and industrial boilers account for over half of these NO_x emissions. Only 15 percent of the stationary NO_x sources are regulated by EPA's New Source Performance Standards (NSPS) [6]; the remainder must be addressed with retrofit technologies if significant NO_x emission reduction is to be realized. Another NO_x control problem is posed by the potential of incinerating high nitrogen content wastes in industrial boilers. While incineration of these materials would not constitute a significant increase in the overall national NO_x emission level, individual plant emissions may be sufficient to result in a local NO_x problem and, thus, prevent on-site incineration from being permitted. With thermal destruction being an attractive alternative to landfill storage of wastes, there continues to be a need for developing high efficiency, low NO_x combustion technologies.

The vast majority of NO_x in stack combustion gas have been found to be NO. Much is known about the mechanisms of NO formation in flames, both from molecular nitrogen (source of thermal NO) and from fuel-bound nitrogen (source of fuel NO). Thermal NO can be reduced by decreasing peak flame temperatures. Fuel NO, not as strongly dependent on temperature, is very sensitive to reactant stoichiometry. Fuel-rich conditions promote N₂ formation over NO formation. Laboratory studies and field test data have established the importance of fuel NO to the total emission of NO_x from residual fuel oil and coal flames. Therefore, minimizing NO_x formation in flames typically involves controlling air and fuel mixing rates to create fuel-rich reducing zones and extracting heat to reduce final oxidation temperatures.

To avoid the need for costly post-combustion NO_x removal, several in-furnace NO_x control strategies have been developed and applied to boilers. These include reduced air preheat, load reduction, low excess air, flue gas recirculation, overfire air, deep air staging, fuel staging (or reburning), and various low-NO_x burner systems [7]. While NO_x emissions can be reduced by 20 to 80 percent using these technologies, from uncontrolled levels exceeding 1000 ppm for some high nitrogen content coals, application of these combustion modifications can result in reductions in combustion efficiency and increases in sooting and slagging in the boiler. This problem is of particular concern in the boiler co-firing of fuels and wastes, where high waste destruction efficiencies and minimal formation of other incomplete combustion products are of paramount importance. The purpose of this work is to investigate various multi-staged combustion concepts for burning high nitrogen fuel/waste streams with low NO_x emissions and high combustion efficiency. Specifically, tests were designed to evaluate the use of an adiabatic precombustion chamber burner, modified to reduce burner size, coupled with air or air/fuel staging. A NO_x emission of less than 0.2 lb (as NO₂)/10⁶ Btu* (or approximately 175 ppm NO_x, measured dry at zero percent O₂) for firing gaseous and liquid fuels doped with up to 5 percent nitrogen (by weight) was targeted. The study is ongoing; in this paper pilot-scale test results are presented on the NO_x emission performances of the proposed firing designs. Future work will evaluate the combustion efficiency performances.

Before describing the experimental procedure and results, some background information is provided.

* The current NSPS for large industrial boilers firing high nitrogen heavy fuel oil is 0.4 lb (as NO₂)/10⁶ Btu. This standard is under review. (1 lb/10⁶ Btu = 0.43 kg/GJ)

Adiabatic Precombustion Chamber Burner

The adiabatic precombustion chamber burner is a staged combustion technology capable of achieving a NO_x emission of less than 0.1 lb (as NO_2)/ 10^6 Btu (or approximately 90 ppm NO_x), even with high nitrogen fuel firing [8]. It consists of a primary air and fuel injection system, a large refractory wall precombustion chamber, and a secondary air injection section. Fuel and primary air are injected for rapid mixing into the nearly adiabatic precombustion chamber with a first-stage stoichiometry of between 0.6 and 0.8.* A residence time between 0.6 and 1.0 s allows for maximum reduction and conversion of fuel nitrogen species to N_2 in the fuel-rich precombustion chamber. First-stage combustion gas products exit the burner through a convergent section which minimizes both radiative heat loss to the boiler and back-mixing of the secondary air. The transition section between the burner and boiler is water-cooled to reduce combustion gas temperatures before final air addition.

The precombustion chamber burner has been tested on a full-scale (16 MW_t) crude oil-fired steam generator used for thermally enhanced oil recovery (TEOR) in Kern County, CA [9]. A 30-day continuous monitoring test demonstrated the burner's ability to maintain a nominal NO emission of 70 ppm and a high combustion efficiency [10]. During burner optimization testing, NO, CO, and smoke emissions were measured over a range of first-stage stoichiometries. These data indicate the sensitivity of NO emission to first-stage stoichiometry and the good hydrocarbon burnout characteristics of the burner. Earlier pilot-scale tests firing nitrogen-free fuels suggest that the minimum NO_x level of about 50 ppm can be attributed to second-stage thermal NO formation.

A test designed to demonstrate the potential for using this burner for nitrogenous waste incineration was performed at EPA's Air and Energy Engineering Research Laboratory. A pilot-scale (0.6 MW) precombustion chamber burner was used to incinerate a surrogate nitrogenous waste mixture of 9.1 percent (by volume) pyridine in fuel oil. A NO emission of less than 100 ppm was maintained, with greater than six nines (99.9999 percent) destruction of the pyridine being achieved. The relative NO emissions with and without pyridine addition indicate that less than 1 percent of the fuel nitrogen was converted to NO. This preliminary result sparked interest in utilizing the precombustion chamber burner for high efficiency, low NO_x combustion.

However, while the precombustion chamber burner has been demonstrated successfully in pilot-scale and field tests, its large size makes it impractical for most boiler retrofit applications. Reducing the burner size results in insufficient first-stage residence time to fully convert the fuel nitrogen to N_2 ; hence, higher NO emissions result. Further NO_x control can be achieved by further staging of the combustion process in the boiler.

Staged Combustion

The concept of staged combustion consists of injecting secondary air into the boiler downstream of the primary combustion zone, which is characterized by substoichiometric levels of combustion air. This concept may be employed by utilizing overfire air ports, secondary air injectors, or burners-out-of-service. In application with a shortened precombustion chamber burner, further air staging would extend the fuel-rich first stage from the burner into the boiler.

Reburning

As many as 30 years ago, experimental results were available indicating that NO could

* The stoichiometric ratio (SR) is defined as the actual air-to-fuel ratio divided by the theoretical air-to-fuel ratio.

be destroyed by reaction with hydrocarbon radicals. Early fundamental studies of NO_x destruction by injection of secondary fuel into the flame zone were performed by Wendt et al. [11], who coined the name "reburning" to describe the process. Concerted effort to develop reburning for application to boilers occurred in Japan during the late 1970's and early 1980's. The first reporting of these efforts was by Takahashi et al. [12], documenting extensive laboratory-, pilot-, and full-scale evaluations of a fuel staging process they refer to as Mitsubishi Advanced Control Technology, or MACT.

Since 1982 EPA has carried out both in-house and extramural bench- and pilot-scale reburning tests. In-house experiments have focussed on natural gas and fuel oil reburning [13-16]. Significant results include quantifying the dependence of reburning effectiveness on primary flame NO level, reburn zone stoichiometry, and reburn fuel nitrogen content. Fifty percent NO reduction was possible with 15 to 20 percent of the fuel used for reburning. At low primary NO levels, however, a nitrogen-free reburning fuel (such as natural gas) must be used to achieve 50 percent reduction. Tests have shown that reburning is effective over a wide range of temperatures and with relatively short reburning zone residence times (0.2 to 0.4 s).

In application with a shortened precombustion chamber burner, reburning would result in a four-stage combustion process. Because much of the primary fuel has been reduced prior to boiler entry, reburning might be applied from the front wall of the boiler. Such reburning application would simplify the boiler retrofit requirement by not requiring multiple boiler penetrations.

EXPERIMENTAL PROCEDURE

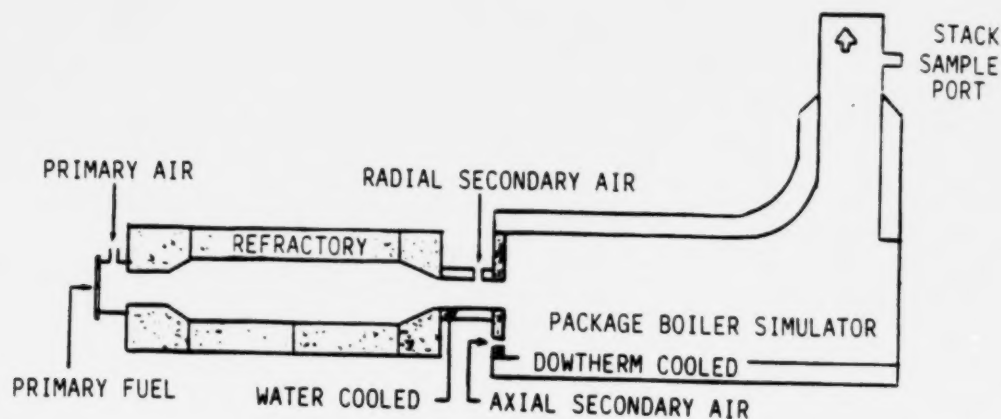
The goal of this study is to minimize NO formation, with an emission target of 175 ppm (dry, at zero percent O₂) or less, and maintain efficient incineration of surrogate fuel/waste mixtures with up to 5 percent fuel nitrogen by using a precombustion chamber burner reduced in size by about half.

The unmodified facility, shown schematically in Fig. 1a, is comprised of a precombustion chamber low-NO_x burner and a package boiler simulator. The precombustion chamber burner consists of a primary fuel and air injection module, two 0.89 m long spool modules with 0.51 m internal diameter, and a 0.33 m long convergent module. These burner modules have a thick refractory wall lining to minimize heat loss, maintaining the high temperatures that promote conversion of fuel nitrogen to N₂ under fuel-rich stoichiometries. To achieve rapid mixing in the precombustion chamber, the primary fuel is injected through a divergent nozzle and the primary air, which is not preheated, is passed through fixed swirl vanes. The convergent module minimizes back-mixing of combustion gas and radiation loss to the boiler. A water-cooled transition module, 0.25 m in internal diameter, cools the combustion gas before secondary air addition to minimize thermal NO generation. Primary fuel nitrogen is simulated by doping ammonia into natural gas or pyridine into distillate fuel oil. All of the results reported here are with the gaseous fuel.

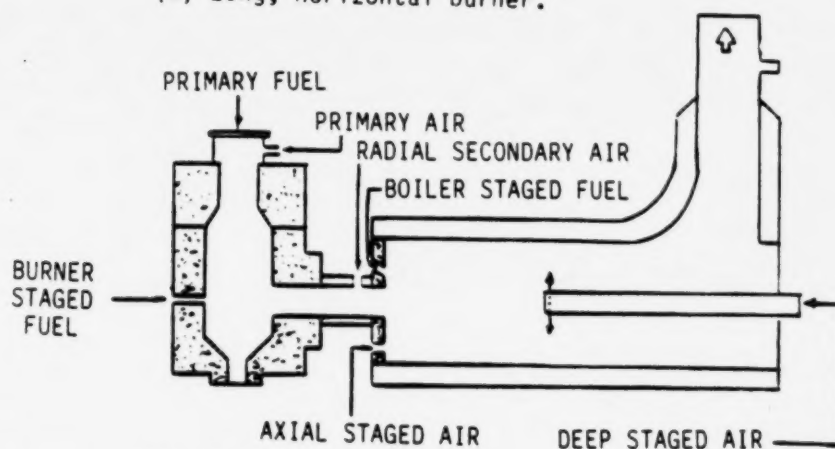
The pilot-scale boiler simulator is rated at 0.9 MW thermal input. The boiler's radiant section is horizontal, 0.6 m in diameter, 3.0 m long, and cooled with Dowtherm G[®] heat transfer fluid. Combustion gas exits the boiler through a vertical stack. The boiler's front face has eight axial ports for addition of staged air.

The research facility was modified as shown in Figure 1b. The horizontal 2.62 m long precombustion chamber burner was replaced with a shorter 1.80 m long vertical burner. This shorter burner, with a nominal residence time of 250 ms, has all the essential design features of the long horizontal burner, which has a nominal residence time of 600 ms. The elbow section has a 5 cm diameter port for staging fuel into the burner. Two of the eight axial air ports on the boiler front face were modified to provide ports for staging fuel into the boiler at an angle of 45 degrees. This design allows for reburning application from the boiler front face, with aerodynamic separation of

the fuel-lean and fuel-rich zones in the boiler. The end plate of the boiler has been modified to allow the insertion of a water-cooled boom for deep staging of air into the boiler.



(a) Long, horizontal burner.



(b) Short, vertical burner.

Figure 1. Pilot-scale combustion research facility. The package boiler simulator has been fitted with a precombustion chamber burner and air and fuel staging ports.

The experimental facility is designed for independent control and measurement of each fuel, fuel dopant, and air stream. Stack gas speciation is measured by a continuous emissions monitoring system. NO and NO_x are measured by chemiluminescence. Reported in this paper are NO measurements only, measured on a dry basis and corrected to zero percent O₂. Spot-check measurements of NO_x indicated that NO emissions accounted for over 95 percent of the exhaust NO_x emissions in these tests.

Evaluated were burner baseline performance and burner operation with various unstaged, air staged, and fuel staged NO controls. The parameters affecting the NO emissions from the facility with unstaged controls are fuel nitrogen content, combustion gas residence time in the prechamber, first-stage stoichiometry, and exhaust stoichiometry. The residence time of combustion gas in the burner depends on precombustion chamber length, load, and stoichiometry. The nominal load was 0.6 MW. The exhaust stoichiometry was kept at a nominal value of 15 percent excess air, as per commercial boiler practice. Nominal fuel nitrogen content was chosen to be 5.8 percent by weight. First-stage stoichiometry was optimized for each NO control application tested.

BURNER BASELINE PERFORMANCE

During burner baseline performance tests, the effects of burner length and first-stage stoichiometry on NO emissions were studied. Three burner configurations, two with a horizontal orientation (residence times of 600 and 350 ms) and one with a vertical orientation (residence time of 250 ms), were evaluated. With each burner configuration, the first-stage stoichiometry was varied by changing the primary and secondary air inputs.

The results of these tests are plotted in Fig. 2. The two dotted curves in the

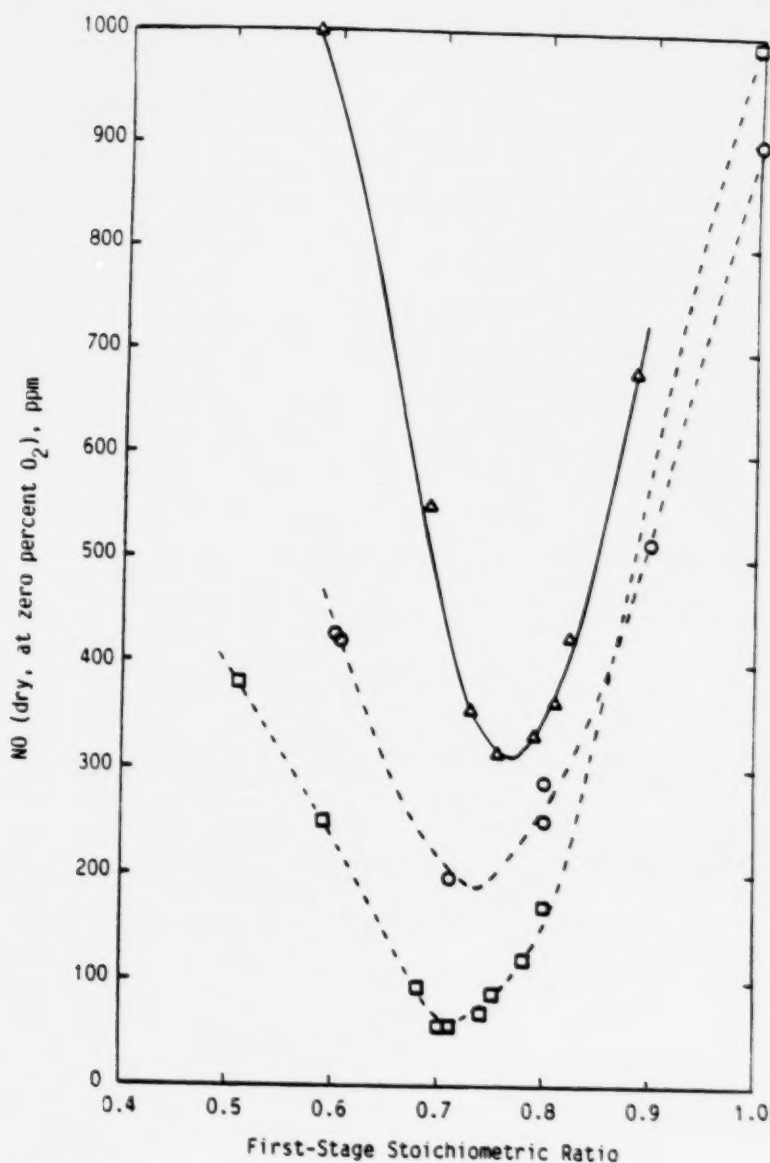


Figure 2. Effect of reduced burner size. The dotted lines represent results from the horizontal burner firing natural gas containing 0.66 percent nitrogen as ammonia. The square symbols correspond to long burner (600 ms) test results; the circles represent short horizontal burner (350 ms) test results. The solid line with triangle symbols shows results with the short, vertical burner firing natural gas containing 5.8 percent nitrogen as ammonia.

figure correspond to the long (two spool modules) and short (one spool module) configurations of the unmodified facility (see Fig. 1a). The solid curve corresponds to the facility configuration used in the rest of this study. The dotted curves show the effect of burner residence time on stack NO levels. The curves indicate a strong sensitivity of stack NO to changes in first-stage stoichiometry. For the long burner configuration, with a residence time of 600 ms, the minimum stack NO concentration was 60 ppm at a primary fuel nitrogen content of 0.66 percent. With the shortened burner configuration, with a residence time of 350 ms, the minimum NO stack concentration rose to 200 ppm at the same fuel nitrogen content. The solid curve was obtained by burning a fuel with 5.8 percent fuel nitrogen (as ammonia) in the vertical burner. A minimum NO emission of 315 ppm occurred at a first-stage stoichiometry of about 0.78. Thus, additional combustion modifications are necessary to achieve the program goal of 175 ppm maximum NO emission.

UNSTAGED NO CONTROLS

Unstaged NO controls included excess air variation, load variation, and co-firing variation. At each test condition, first-stage stoichiometry was optimized by adjusting the appropriate air flow rates. For the co-firing tests, the ammonia dopant level in the fuel stream was varied to simulate the situation of co-firing a nitrogen-free fuel (natural gas) with surrogate waste containing 5.8 percent nitrogen.

Excess Air Variation Results

The effect of excess air variation on stack NO is shown in Fig. 3. Decreasing excess air from 15 to 5 percent reduced the exhaust NO from 315 to 290 ppm. NO emission increased only slightly beyond an exhaust stoichiometry of about 1.2. While reducing excess air did provide some NO reduction, maintaining an exhaust excess air level of 15 percent is important for achieving high combustion efficiency.

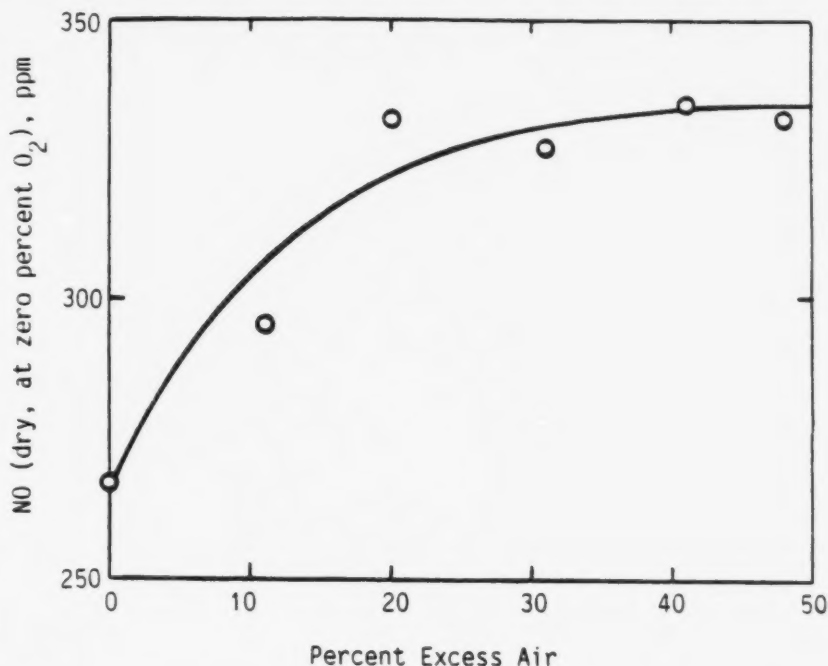


Figure 3. Excess air variation results.

Load Reduction Results

The effect of load reduction on stack NO is shown in Fig. 4. As load was decreased

from a nominal condition of 0.6 MW to 65 percent of nominal, the stack NO concentration dropped from 315 to 260 ppm. Load reduction corresponds to an increase in residence time and, thus, a decrease in NO emission. Reducing load by 35 percent increased burner residence time from 250 to 410 ms. However, boiler steam requirements may make load reduction an impractical means of NO_x control.

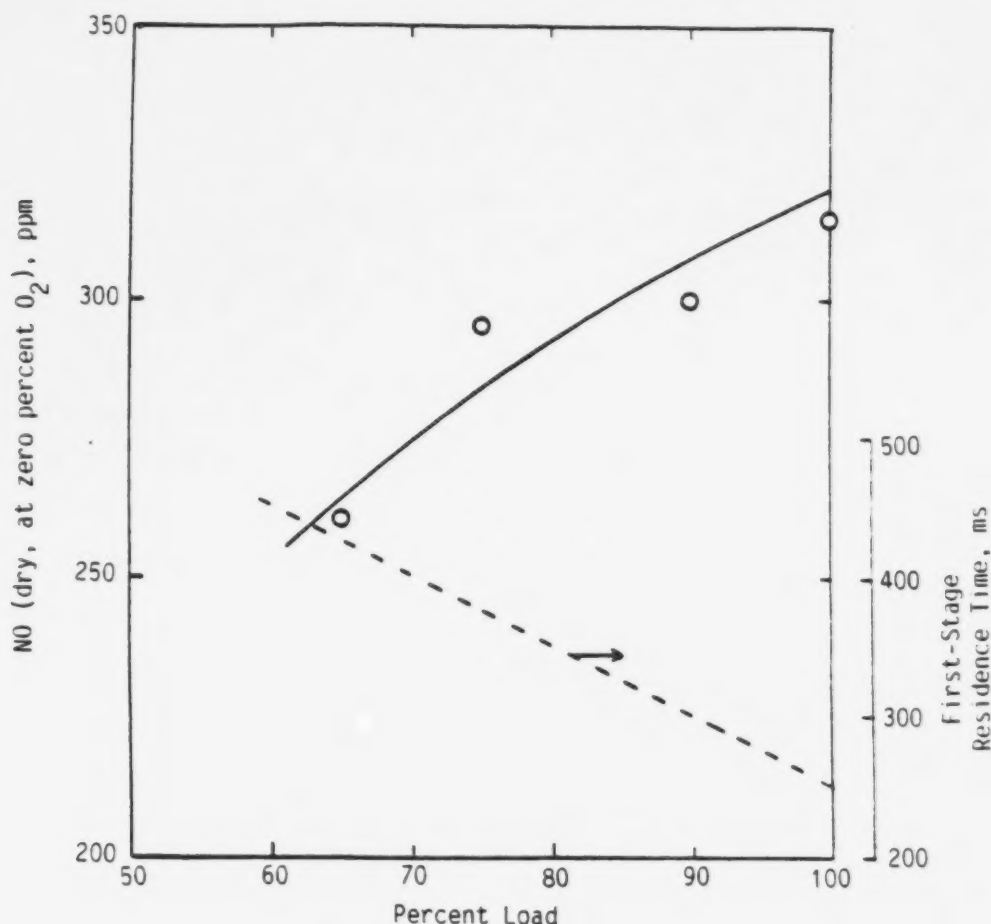


Figure 4. Load variation results.

Fuel/Waste Co-Firing Results

The effect of co-firing a nitrogen-free fuel (natural gas) and a surrogate nitrogenous waste (ammonia-doped natural gas) with 5.8 percent nitrogen is shown in Fig. 5. Data are plotted for the full range of co-firing conditions, from 100 percent fuel to 100 percent surrogate waste. Exhaust NO level increased with increasing fuel nitrogen content in the fuel/waste stream, as expected. However, exhaust NO levels became less sensitive to fuel nitrogen content above 3 percent, with emissions peaking at less than 350 ppm. It should be noted that, for conventional unstaged combustion, NO emission would be expected to exceed 1000 ppm for firing a fuel with a nitrogen content of more than 5 percent.

AIR STAGED NO CONTROLS

During air staged NO control tests, the effect of moving the location of secondary air addition, from the radial ports in the transition section to the axial and deep staged ports in the boiler, was examined. The secondary air was distributed between

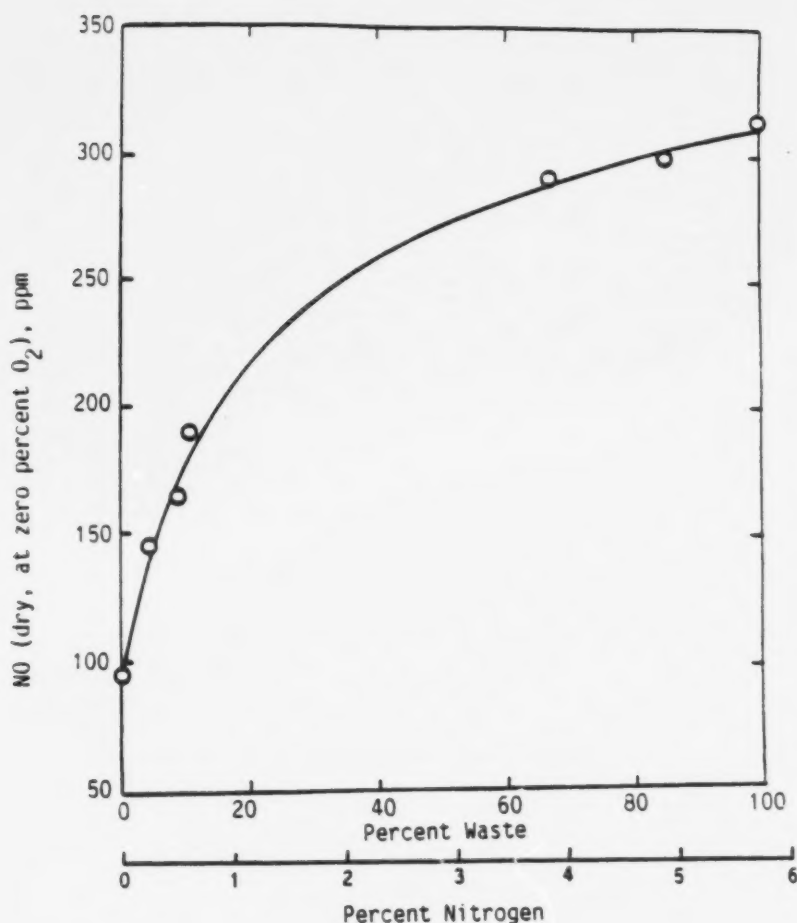


Figure 5. Fuel/waste nitrogen variation results.

radial and axial locations in one series of staging tests, and between radial and deep staged ports (located 132 cm from the boiler front face) in a second series of tests. This created a three-stage combustion process: a fuel-rich burner zone, a less fuel-rich (SR₂) zone after radial secondary air injection in the transition section, and a fuel-lean burnout zone after final air addition. A water-cooled boom, aligned with the centerline axis of the boiler, was used to supply the deep staged air. As in the previous tests, first-stage stoichiometry was optimized at each test condition.

Test results for the two cases of secondary air staging in the boiler are shown in Fig. 6. The axial air staging results show a drop in minimum NO concentration from 315 ppm with no staging to 220 ppm with 100 percent of the secondary combustion air moved from the radial injectors to the axial injectors. The temperature of the combustion gases was higher in the transition section than in the boiler; also, the mixing of secondary air and combustion gas was more rapid when the secondary air was added radially. Hence, more thermal NO was generated and more fuel nitrogen species fragments were oxidized with radial air addition into the transition section than with axial addition into the boiler. Similarly, lower temperatures in the boiler at the deep staged air location and longer fuel-rich zone residence time resulted in a lower NO emission when the secondary air was deep staged. With all of the secondary air being added from the deep staged location, the minimum NO level was 160 ppm.

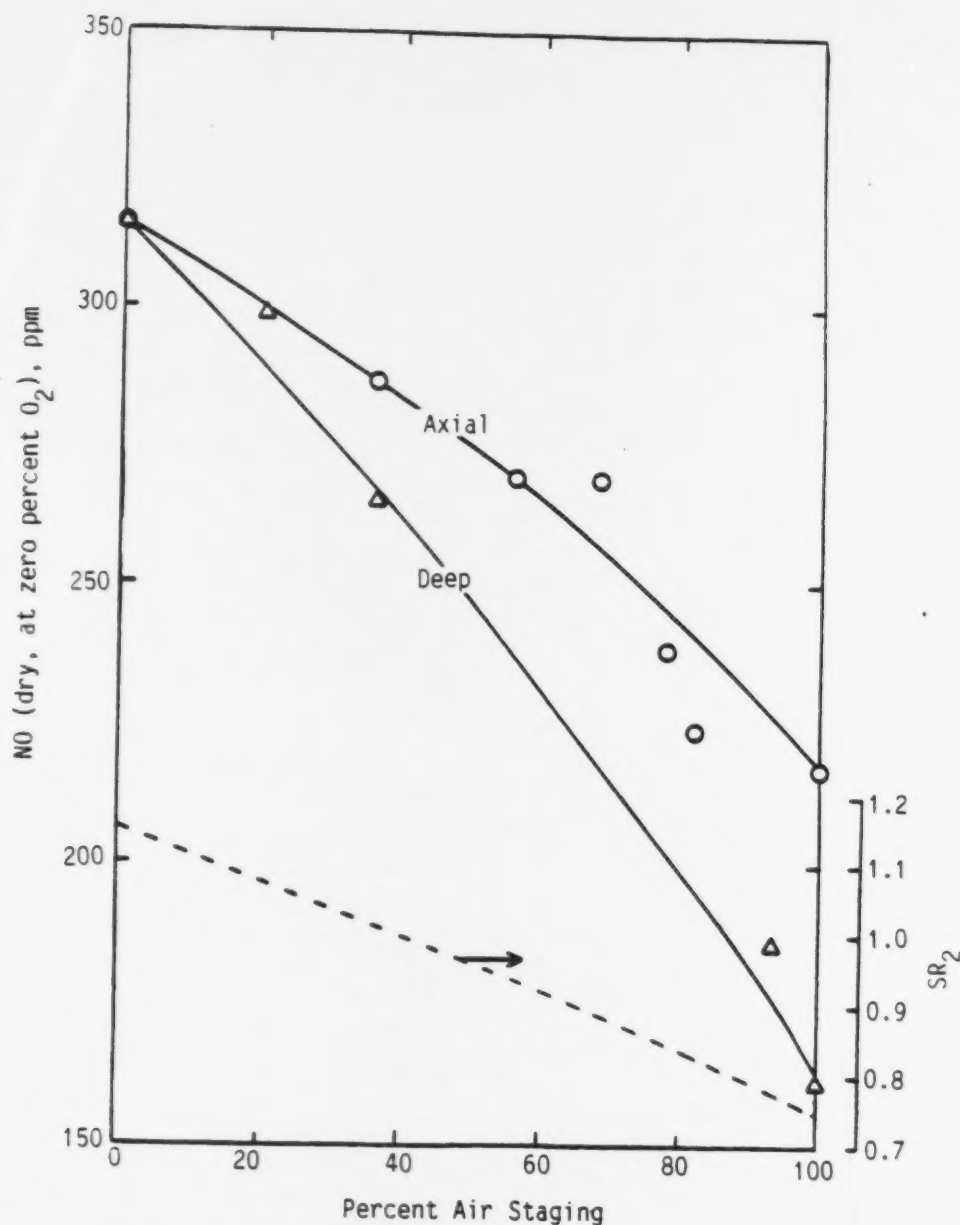


Figure 6. Air staging results.

From the test results just described, deep staging of secondary air is shown to be an effective means of minimizing NO emissions. However, such staging may lead to burnout problems, which is of great concern when co-firing waste. Extending the fuel-rich zone from the precombustion chamber into the boiler exposes the reducing combustion gases to cool boiler walls, which may result in slagging and/or sooting. Further, the lower combustion gas temperatures in the boiler slow the fuel-rich nitrogen kinetics.

FUEL STAGED NO CONTROLS

During fuel staged NO control tests, the effect of diverting part of primary fuel to staged locations in the burner and boiler was studied. The staged fuel was natural

gas, with no ammonia dopant. The first-stage stoichiometry was optimized with respect to NO emission. In the case of fuel staging in the burner, the secondary natural gas was added, using a water-cooled injector, down the centerline axis of the boiler; secondary air was added axially into the boiler to allow sufficient fuel-rich zone residence time. In the case of fuel staging in the boiler, the secondary natural gas was added at an angle of 45 degrees, using watercooled injectors, from two ports in the boiler front face. Secondary air to complete primary fuel combustion was added radially into the transition section, while burnout air for secondary fuel combustion was added axially near the boiler wall, using six axial ports on the boiler front face.

Burner Fuel Staging Results

Holding total load constant, fuel was diverted from the primary fuel injector to a secondary injector near the precombustion chamber exit (see Fig. 1b), thus creating two stoichiometric zones in the burner in addition to the burnout zone in the boiler. The staged fuel (undoped natural gas) provided a burst of hydrocarbon radicals that accelerated the reduction of primary fuel nitrogen to N_2 prior to secondary air injection. Secondary air was injected through the axial injectors. The results, plotted in Fig. 7, show a decrease in NO emission with increasing fuel staging. Two effects contribute to this decrease in NO emissions with fuel staging: (1) fuel nitrogen reduction mechanisms are accelerated due to increased radical concentrations, and (2) combustion gases from the high nitrogen content primary fuel are diluted by the combustion gases from the nitrogen-free secondary fuel. With 35 percent of the fuel staged, the exhaust NO levels decreased to 190 ppm, from 220 ppm with no fuel staging (and axial secondary air addition). The figure also shows that the optimum first-stage burner stoichiometry (SR_1) increased with increasing fuel staging, while the optimum second-stage burner stoichiometry (SR_2) decreased slightly. This result is consistent with kinetic model predictions of optimum stoichiometries for the two burner stages. A first-stage stoichiometry of 90 percent theoretical air should result in a higher destruction efficiency of the primary fuel/waste stream than with a more fuel-rich first stage.

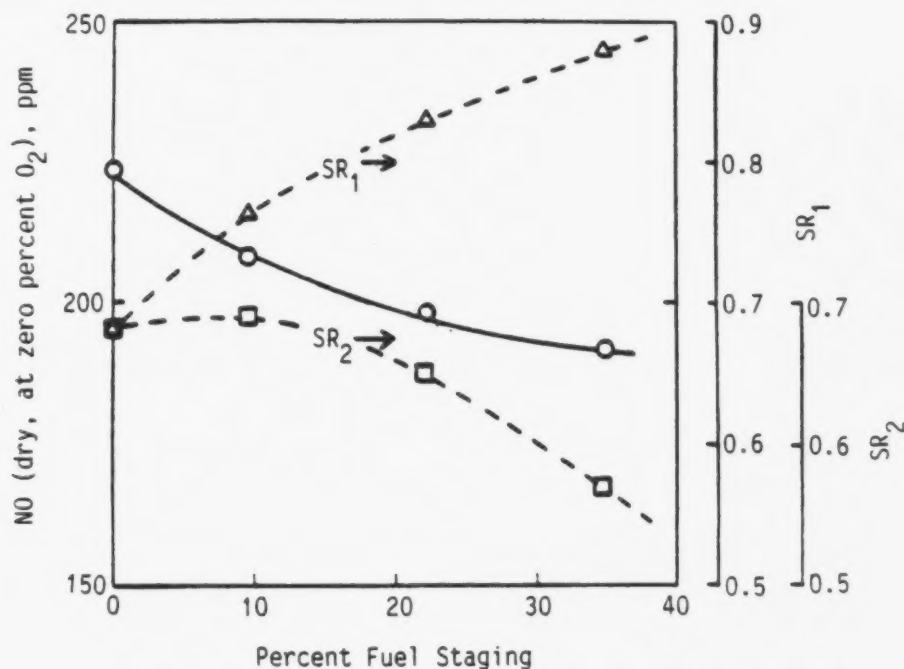


Figure 7. Burner fuel staging results.

Boiler Fuel Staging Results

As in the tests just described, total boiler load was held constant while fuel was diverted from the primary fuel injector to a secondary injector. In this case, the staged fuel (undoped natural gas) was injected into the boiler downstream of the secondary radial air addition. Thus, a four-stage combustion process was established, consisting of a fuel-rich burner zone and three boiler zones characteristic of reburning (i.e., fuel-lean, fuel-rich, fuel-lean). The stoichiometry in the third stage (SR₃), the fuel-rich reburning zone in the boiler, is critical in this NO control process. As already described, all of the staged air and fuel flows were injected from the front face of the boiler at various angles, resulting in the three boiler stoichiometric zones. Figure 8 shows that NO emissions decreased with increased fuel staging. This was due to both primary NO destruction and primary combustion gas dilution. Two second-stage stoichiometries (SR₂) were established: 1.1 and 1.0. With 35 percent fuel staging, the exhaust NO levels were reduced to 195 ppm (from 315 ppm) at a SR₂ of 1.1 (and a SR₃ of 0.72) and to 160 ppm at a SR₂ of 1.0 (and a SR₃ of 0.65). Due to less distinct stoichiometric zones than typically established in reburning application, the NO reduction by fuel staging was not quite as great as that obtained when the staged fuel was injected farther downstream of the fuel-lean primary combustion zone [12]. However, the configuration used in these tests required no boiler penetrations. With this multistaged combustion, the NO emission goal of less than 175 ppm was achieved. In addition, complete destruction of the primary fuel/waste stream appears to be ensured by providing all of the required primary combustion air prior to entry into the boiler, and then passing the primary combustion gases through a secondary flame.

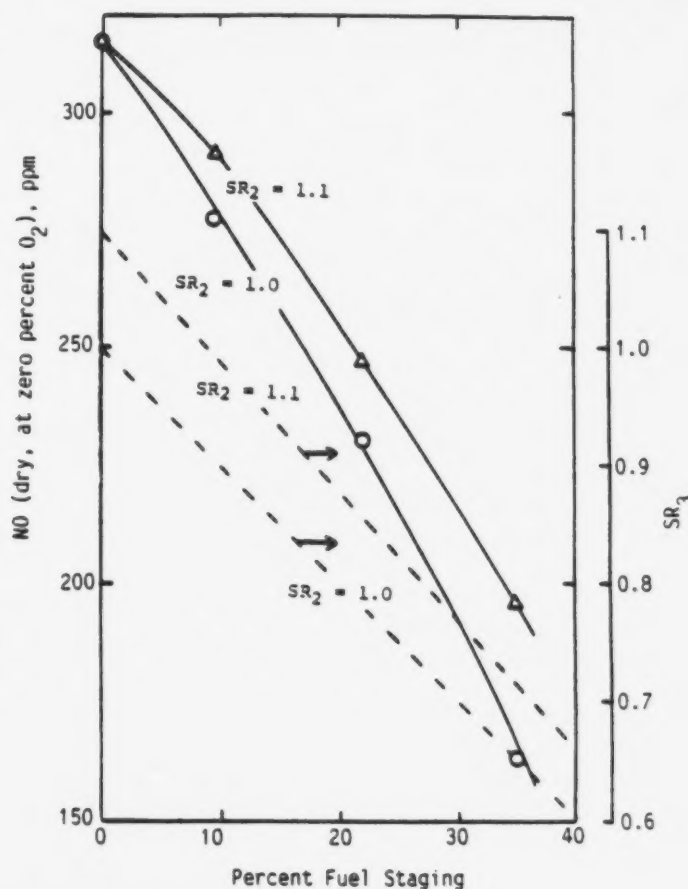


Figure 8. Boiler fuel staging results.

DISCUSSION AND CONCLUSIONS

Table I summarizes results from the various combustion modification schemes for the reduction of NO. These results were obtained at optimal first-stage stoichiometries. From the table it can be seen that deep air staging and fuel staging in the boiler are most effective in minimizing NO emission. However, deep air staging not only presents problems of hardware modification due to boiler penetrations, but may also lead to inefficient combustion. A CO concentration in the fuel-rich boiler zone of 2.75 percent was measured for the deep air staged test condition. On the other hand, the boiler fuel staging hardware modifications used in this study were designed with retrofit feasibility and efficient combustion in mind. In the tests described here, all of the secondary combustion air necessary for primary fuel burnout was introduced with rapid mixing at high temperatures in the water-cooled transition section between the burner and boiler. Further, staged fuel and air from the front face of the boiler provided a secondary flame for increased primary fuel/waste destruction, similar to incinerator afterburners.

TABLE 1. SUMMARY OF RESULTS

Control Modification	Stoichiometric Ratio				CO (boiler)	NO (stack)
	Burner	Transition	Boiler	Stack		
Burner Baseline						
-Long (600 ms)	0.73	1.15	1.15	1.15	----*	90 ppm
-Short (250 ms)	0.78	1.15	1.15	1.15	35 ppm	315 ppm
Unstaged Control						
-Excess Air Reduction	0.78	1.05	1.05	1.05	150 ppm	290 ppm
-Load Reduction (35%)	0.78	1.15	1.15	1.15	----*	260 ppm
-Fuel N ₂ Reduction (35%)	0.78	1.15	1.15	1.15	----*	295 ppm
Air Staged Control						
-Axial	0.75	0.75	1.15	1.15	0.25%	220 ppm
-Deep	0.75	0.75	0.75	1.15	2.75%	160 ppm
Fuel Staged Control (35%)						
-Burner	0.89	0.56	1.15	1.15	0.55%	190 ppm
-Boiler						
-SR ₂ =1.1 (SR _P =0.72)	0.78	1.10	1.15	1.15	0.10%	195 ppm
-SR ₂ =1.0 (SR _P =0.65)	0.78	1.00	1.15	1.15	0.50%	160 ppm

*No measurement taken.

Some mention should be made of the limitations of these results. First, little information has been collected to date on surrogate fuel/waste burnout. Burning natural gas and ammonia mixtures, rather than the liquid fuel/waste mixtures and pulverized coals that are encountered in practice, allows for well-controlled parametric testing for NO emission evaluation, but does not provide for good burnout simulation. Stack emissions of CO were less than 10 ppm for every test condition reported here. However, in-furnace CO sampling provided some insight into the potential for fuel burnout problems. Another problem with testing with natural gas is the simplified mixing processes and faster kinetics characteristic of gaseous fuel combustion. NO emissions from the shortened precombustion chamber burner would tend to be lower for natural gas firing than for the firing of fuels and wastes that require vaporization or pyrolysis. Fuel oil tests are needed to confirm the NO emission measurements and limited carbon burnout measurements reported here.

Another limitation of this study is that the results are applicable only in the range of temperatures characteristic of the firetube package boiler. Temperatures in the package boiler simulator ranged from 1700 K at the boiler entry to 1250 K at the boiler exit. To avoid high thermal NO formation in the primary combustion gas burnout, sufficient heat must be extracted in the transition section to lower the combustion gas temperatures to less than 1800 K.

Finally, it should be noted that the low NO emissions from the fuel staging tests are achieved largely by dilution of the primary combustion gases with secondary flame gases, which do not have a fuel nitrogen input. Actual molar destruction of NO is small in these tests. However, this dilution is coupled with the NO formation and destruction processes and should not be discounted. From the standpoint of NO minimization and fuel/waste destruction maximization, overall emissions per unit mass of input should be considered. From this perspective, fuel staging in combination with the shortened precombustion chamber burner appears to be the most attractive combustion modification for high nitrogen content fuel/waste firing in boilers.

Further characterization of this multistaged burner design is ongoing at EPA. Fuel burnout is being measured to optimize both combustion efficiency and NO emission. Pyridine and fuel oil mixtures are being used for this study.

ACKNOWLEDGMENT

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DIESEL ENGINE NO_x CONTROL:
SELECTIVE CATALYTIC REDUCTION
AND METHANOL EMULSION

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ABSTRACT

EPA's Air and Energy Engineering Research Laboratory has recently conducted two diesel engine NO_x reduction studies, one a long term test evaluation of a selective catalytic reduction (SCR) system and the other an evaluation of methanol emulsion fuel. The SCR project established the NO_x reduction performance of a catalytic unit over a 4000-hour period. NO_x reductions ranged between 98 and 69% during the test, with periodic (approximately every 1300 hours) dry cleaning required to maintain activity. Measurements of other pollutants (carbon monoxide and particulate matter) indicated that the catalyst and/or ammonia addition had no effect on these emissions. No adverse operational problems were encountered on the engine system during the test program. The methanol project established the performance of this fuel modification. The diesel system was equipped with a fuel emulsification unit capable of delivering methanol/fueloil or water/fueloil mixtures to the engine's fuel supply line. NO_x emission reductions of 20 to 25% were measured when firing methanol/fueloil emulsions compared to fueloil firing only. However, substantial increases in carbon monoxide (from 30 to 700 ppm) and hydrocarbon (from 4 to 200 ppm) emissions were also recorded. The methanol/oil emulsion results are also compared to water/oil emulsion results on the same engine.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

NOMENCLATURE

btdc	before top dead center	mm	millimeter
Btu	British thermal unit	M/F	methanol/fueloil
CO	carbon monoxide	NDIR	non-dispersive infrared
FID	flame ionization detector	NO _x	nitrogen oxides
HC	hydrocarbons	O ₂	oxygen
kW	kilowatt	ppm	parts per million
L	liter	rpm	revolutions per minute
Lph	liters per hour	W/F	water/fueloil

INTRODUCTION

The Combustion Research Branch (CRB) of EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, N.C., sponsors contract and in-house R&D programs to investigate emission control technology for stationary reciprocating internal combustion engines. This paper will describe the results obtained for two in-house research projects: one a long-term (4000 hour) durability test with a full-stream ammonia/ NO_x reduction catalyst installed in the exhaust system of a diesel engine, the other a substitution of methanol (methyl alcohol) for part of the fuel injected into a diesel engine.

The purpose of the first project was to establish both the initial and 6-month operation equivalent effectiveness of a selective catalytic reduction (SCR) system in the hostile diesel exhaust environment. Results of this test will provide support to EPA Region 9 and California air pollution control authorities in carrying out their regulatory responsibilities.

The purpose of the second project was to examine the potential effects on NO_x , CO, HC, and particulate emissions if a nonpetroleum derived fuel were to be used to conserve petroleum based fuels in the future.

QUALITY ASSURANCE

Since April 1984, EPA research and development projects have been performed under a mandatory Quality Assurance Program. This program recognizes four descending levels of QA stringency, Categories I through IV. Each R&D project is assigned to an appropriate category to ensure adequate quality for the intended use of the resultant data. The projects described in this paper, while initially predating the mandatory requirements, followed the Category IV (Basic R&D) level specification until the final test series for the catalyst test. This series was elevated to the Category I level. Performance and systems audits were performed at appropriate points during the final stages of testing the catalyst by an independent third party (Research Triangle Institute) to certify the degree of success in matching the QA goals. The final data (performance after 3900 hours) were actually taken under an approved Level I QAPP.

Most of the data reported in this paper were obtained under research operating procedures which essentially followed the instrument manufacturer's specifications. Manufacturer's span gas analyses were used to establish instrument calibration, but were not certified against known standards. An independent audit of the data acquisition operation was not made. Thus, the data quality is sufficient only for understanding direction and order of magnitude of modification effects on system emissions, but would be well short of supporting regulatory or policy operations. The final catalyst test data are fully supportable.

SAMPLING AND ANALYTICAL SYSTEM

The sampling and analytical equipment/methods used in these programs, for the most part, were the standards established over the past 20+ years of conducting combustion research by CRB. The following is a description of the equipment and procedures involved. Gaseous emission analytical instruments consisted of two Beckman Model 865 NDIR analyzers for CO and CO_2 , a Beckman Model 755 paramagnetic analyzer for O_2 , a Model 415 Scott FID-type total hydrocarbon analyzer, and a Thermo Electron Model 10A chemiluminescent NO_x analyzer. A molybdenum converter and a heated capillary module have been added to the NO_x unit to provide NO , NO_2 , and NH_3 measurement capability. The output signals from each of these instruments is connected to dual-pen Model L1102S Esterline-Angus chart recorders for permanent

data storage. Exhaust gas samples to all gaseous emission analytical instruments are filtered through a common Balston in-stack stainless steel filter. For the SCR test, the sampling point was located approximately 7 ft (2.1 m) downstream from the catalyst outlet. An upstream sampling point was also available for before-catalyst measurements. The same point was used for the methanol study, but the catalyst unit was replaced with a straight pipe section.

Particulate matter emissions were determined with a standard EPA Method 5 sampling train manufactured by Research Appliance Corp. The sampling point was located in a vertical stack section approximately 10 ft (3 m) downstream from the catalyst outlet. It was not possible to probe upstream of the catalyst for the particulate sample, thus the catalytic unit had to be removed from the exhaust line for without-catalyst sampling runs.

Ammonia (NH_3) measurements were made using several different techniques. Outlet concentrations were measured by the TECO NO_x analyzer (in NH_3 mode), an ion-specific electrode method (ISE), and Kitagawa or Draeger tubes. Inlet NH_3 was controlled by a mass flow meter, and amounts injected were confirmed by continuous mass/weight measurements.

EXPERIMENTAL SYSTEM COMPONENTS

The diesel engine used for both studies is part of an electrical generator set. It is a Caterpillar Model D334, prechamber ignition, turbocharged, after-cooled, four stroke cycle, six cylinder diesel rated at 165 kW output. Other pertinent specifications include:

Bore: 120 mm
Stroke: 152 mm
Displacement: 10.5 L

Compression Ratio: 17 to 1
Standard Timing: 8° btdc
Speed: 1800 rpm (constant).

Engine load is provided by an Avtron Model K463 load bank. This unit provides load demands up to 225 kW in 5 kW increments.

Fuel oil used in both studies was a No. 2 diesel oil with an API (American Petroleum Institute) gravity of 33.6, cetane index of 42.6, and a HHV of 36508 Btu/L. It was commercially available in North Carolina.

Technical grade methanol with an API gravity of 46.2 and a HHV of 15947 Btu/L was obtained in 208 L (55-gal.) drums for that study. Water used in previous emulsion studies referred to in this paper for comparison with methanol performance was deionized city water; thus it was essentially pure H_2O .

An emulsion unit previously developed for water/fuel mixture preparation was used to handle methanol/fuel mixture preparation. This unit provides calibrated rotometer measurement of both fuel/oil/ and methanol/water feed, and a gear pump for emulsifying the mixtures and supplying them to the engine fuel injectors.

A nominal phosphorus-free lube oil was used to prevent catalyst poisoning. However, analysis indicated that some natural phosphorus is present in the lube oil.

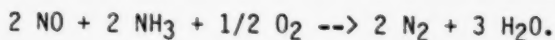
Specific to the SCR study, The Engelhard Torvex™ Catalytic Abatement System has been designed to reduce NO_x emissions from a stationary, lean-burn diesel

engine. The catalyst is housed in a stainless steel shell consisting of two end cones and a square cross-section center section. Catalyst material used on the monolith is a proprietary formulation. Internal aerodynamic design of the catalyst unit was specific for the particulate-laden exhaust gas normally encountered in a diesel engine.

The ammonia delivery system consisted of a 150 lb (68 kg) supply cylinder and regulator, mounted on a scale, and a Brooks mass flow meter for injection rate measurement. Ammonia was injected into the exhaust pipe with a 0.25 in. (6.35 mm) stainless steel nozzle. The injection nozzle has four radial holes and one axial hole to provide adequate injection distribution. Ammonia injection was located at two different points during the test series, 3 ft (0.9 m) and 6.5 ft (2 m) from the catalyst. There was no performance difference measured at either location.

SCR PROCESS

In a typical diesel engine, the exhaust NO_x concentration substantially exceeds the chemical equilibrium concentration which would be thermodynamically predicted for the temperature and other conditions existing in the exhaust manifold. The NO_x is out of equilibrium because, after high concentrations are formed in the combustion chamber, the decomposition reaction paths to N_2 and O_2 are relatively slow. It is conceptually possible to reduce the NO_x levels by stimulating reactions which decompose NO_x into non-pollutants. One important reaction mechanism involves combining ammonia (NH_3), O_2 , and NO_x to produce N_2 and water. This overall reaction is:



There are two approaches to using this reaction to control NO_x . At high temperatures (1240K/1770°F) the reaction will proceed rapidly in the gas phase. This approach would not require a catalyst, but engine exhaust is normally well below the needed temperature, thus requiring costly reheating of the exhaust gas. NO_x reductions expected for this approach are only in the 50-60% range, eliminating consideration of this approach.

The alternate catalytic approach was chosen, even though expensive for catalyst purchase, because the temperature range more closely matches diesel exhaust levels and (most importantly) the expected NO_x reductions are in the 80-90% range. Less ammonia is used by the catalytic approach as the NH_3/NO_x ratio is about 1.1:1 rather than the 2.0:1 expected for the high temperature approach.

EXPERIMENTAL APPROACH: SCR

Baseline emissions characteristics were established for an engine load range from 20 to 165 kW prior to installation of the test catalyst. Based on exhaust temperature data from the engine and the manufacturer's specified catalyst operating range (575 to 825°F; 302 to 441°C), the engine/catalyst test range was defined as 50 to 110 kW. A midpoint at 80 kW was selected for continuous operation of the engine/catalyst system because NO_x emissions are relatively high (approx. 400 ppm) and particulate emissions are typical (30 mg/m³) at that condition. The catalyst temperatures at 80 kW were: inlet @ 785°F (418°C) and outlet @ 715°F (379°C). The system duty cycle set for the test consists of 24-hour-a-day operation at 80 kW for 5 days per week. Thus, the engine is shut down and restarted once each 100 hours of operation. The catalyst is subject to very high particulate loadings (120 mg/m³) at each start-up. The test plan included varying the NH_3 injection rate at selected points in time during the test to confirm the continued NO_x reduction performance of the system.

SCR DATA AND RESULTS

Catalyst NO_x emission/reduction data are presented in Table 1. Data were obtained at varying intervals over the 16-month period required to log 4000 hours on the catalyst using the intermittent test schedule. NO_x emission data are plotted in Figure 1, illustrating the difference between baseline NO_x (before the catalyst) and NO_x emissions at the catalyst outlet. The catalyst was successful in controlling NO_x levels well below 100 ppm over the operating period. Figure 2 is a plot of NO_x reduction with time over the 4000-hour test range. This figure illustrates the effect of cleaning the catalyst when performance deteriorates, and the area under the curve is a measure of the relative amount of NO_x eliminated.

Emissions of carbon monoxide are listed in Table 2. Averages for each condition were computed and found to be virtually identical. The data are plotted in Figure 3, illustrating the data scatter and the fact that the catalyst and/or ammonia have no effect on the CO levels. Hydrocarbon concentrations were too low (10 to 20 ppm) to determine any effect on them by the catalyst, thus they were not reported. Emissions of NO_2 never exceeded 5 ppm and therefore are not reported. Particulate emissions with the EPA Method 5 were:

0.0226 g/dscm	@ catalyst + NH_3
0.0300 "	@ catalyst only
0.0290 "	@ no catalyst

Within the normal variability expected from the particulate train, these emissions do not appear to be significantly affected by the catalyst. Since the catalyst does accumulate particulate matter, the catalyst acts as a collection device. However, the collection efficiency must be very low because the data do not indicate a significant effect. If the catalyst were an efficient collector, it would plug much faster than the 1000+ hours experienced during the test period.

CONCLUSIONS: SCR

1. The Engelhard catalyst was successful for 4000 hours in reducing NO_x emissions by an average of 87% from a diesel engine.
2. After long term exposure to particulate-laden diesel exhaust, the catalyst could be restored to better than 91% NO_x reduction performance. This indicates that no significant poisoning process was affecting the catalyst in this service.
3. The major problem involved with applying a SCR catalyst in diesel NO_x control is the effect of particulate deposition within the catalyst matrix, specifically blocking the front face openings of the monolith. An improved design for lower particle collection or an upstream particulate control device would eliminate the periodic cleaning requirement.
4. Cleaning frequency will depend on the individual engine particulate emission pattern, especially on operating time at the highest particulate levels. This will have an important effect on the cost-effectiveness of applying this technology.
5. The operating temperature range limitations of the tested catalyst will also be a problem in practical application. A wider temperature range would be required or exhaust cooling will be needed to protect the catalyst at high engine load where temperatures might exceed 850°C.
6. This test represents only one catalyst/engine system combination. Further

evaluation of catalysts on different engines would be necessary to establish this technology as a state-of-the-art control method.

EXPERIMENTAL APPROACH: METHANOL

Two series of experiments were designed to evaluate emissions from the diesel engine when methanol was used in a mixture with No. 2 oil. The first series involved three engine load levels and six methanol levels as indicated in the following matrix:

Load(kW)	Methanol Levels(Lph)					
	0.0	7.6	14.8	22.3	29.9	37.1
80	X	X	X	X		
120	X	X	X	X	X	X
160	X				X	

At each indicated test point, emissions of NO_x , CO, and HC were continuously monitored along with the fuel consumption and oxygen levels. The data are recorded in Table 3.

The second series involved four timing levels and two methanol levels at one load level(160 kW) as indicated in the following matrix:

Methanol(Lph)	Timing Levels($^\circ$ btdc)			
	4.5	5.6	6.8	8.0
0	X	X	X	X
30	X	X	X	X

At each indicated test point, emissions of NO_x and particulates were measured along with the fuel consumption and oxygen levels. These data are recorded in Table 4.

METHANOL DATA AND RESULTS

Methanol and load effects on NO_x emissions are presented in Figure 4. As the proportion of methanol in the fuel mixture increased, NO_x emissions decreased slowly. The effect was most pronounced at high load (160 kW), with shallower slopes at lower load levels. Comparing methanol NO_x reductions with water reductions obtained in a prior study¹ indicated that water had a far greater effect. Figure 5 illustrates the difference between the two. The methanol trend levels out at 25% reduction after a 1:1 ratio is reached, while the water trend continues to reduce NO_x by up to 80%.

Methanol substitution also has an effect on other emissions. As Figures 6 and 7 illustrate, CO and HC emissions tend to increase slowly as the proportion of methanol increases. However, at the low load condition (80 kW), CO experienced a large increase above a ratio of 0.6. Again comparing the methanol and water experiences, Figure 8 indicates they have similar effects except at low load, where methanol produces a large increase in CO emissions.

Methanol and timing effects on particulate emissions are illustrated in Figure 9. For a fixed methanol level, delaying ignition from the standard 8 to 4.5 $^\circ$ btdc creates an increase of 30% in particulates. Figure 10 indicates a decrease of 9% in NO_x emissions for the same timing change. These figures also indicate that both NO_x and particulate emissions are reduced by methanol substitution.

Fuel efficiency data are presented in Table 5. The effect of methanol on energy consumption is illustrated in Figure 11. At low load (80 kW), methanol addition increases the fuel consumption required to maintain constant power output. At high load (160 kW), the reverse situation results: methanol addition decreases the total fuel required. At the intermediate load (120 kW), no significant changes are evident.

CONCLUSIONS: METHANOL

1. Methanol substitution for No. 2 fuel oil up to or exceeding equal volumes reduces NO_x emissions by up to 25% in a diesel engine. This is a much less effective method than water emulsification which creates reductions of up to 80%.

2. Methanol substitution increases CO and HC emissions significantly; however, a 42% decrease in particulate levels can be obtained.

3. Ignition retard can produce small NO_x reductions (9%), but at the expense of a 30% increase in particulates.

4. Fuel efficiency appeared to improve at full engine load, but was reduced or unchanged at lower load levels.

REFERENCE

1. Wasser, J.H., Emulsion Fuel and Oxidation Catalyst Technology for Stationary Diesel Engines. In: Proceedings of the 1982 Joint Symposium on Stationary Combustion NO_x Control, Vol. 2, EPA-600/9-85-022b (NTIS PB85-235612), pp. 40-1 to 40-18, July 1985.

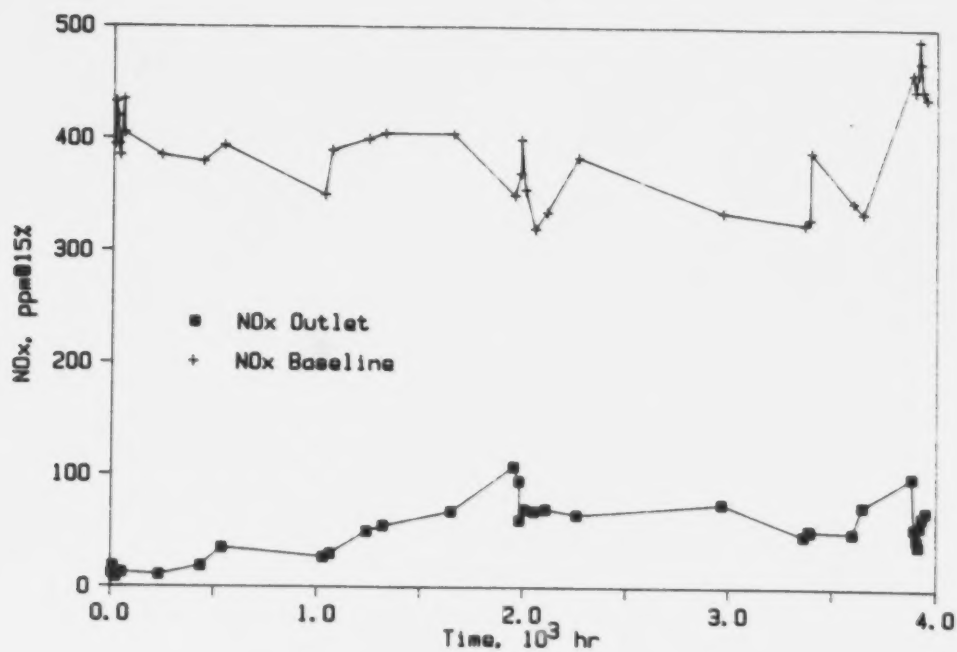


Figure 1. NOx emissions, diesel catalyst tests.

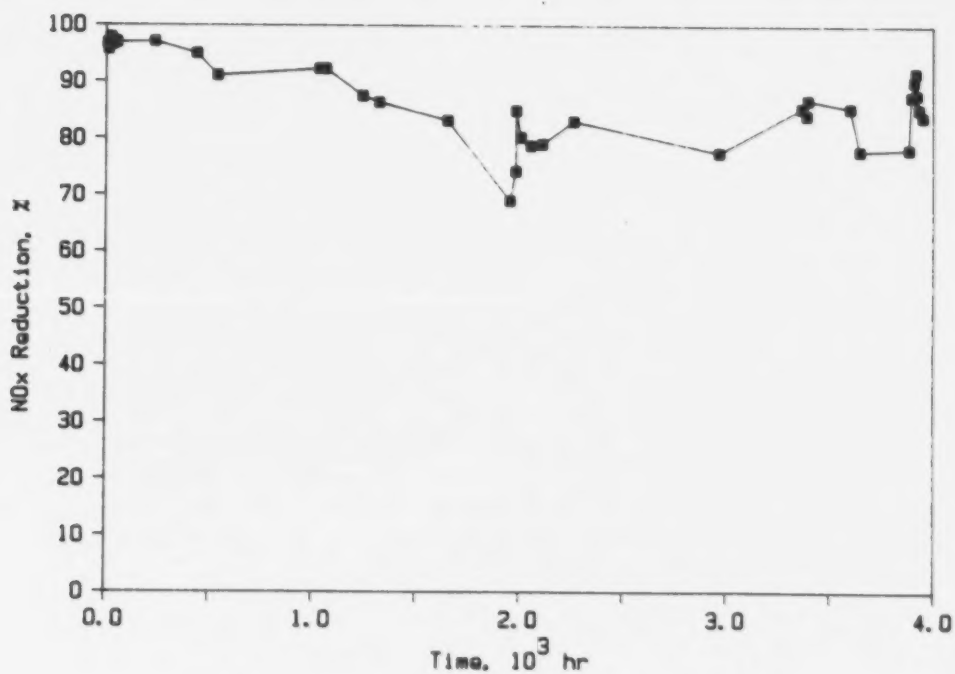


Figure 2. NOx reduction, diesel catalyst tests.

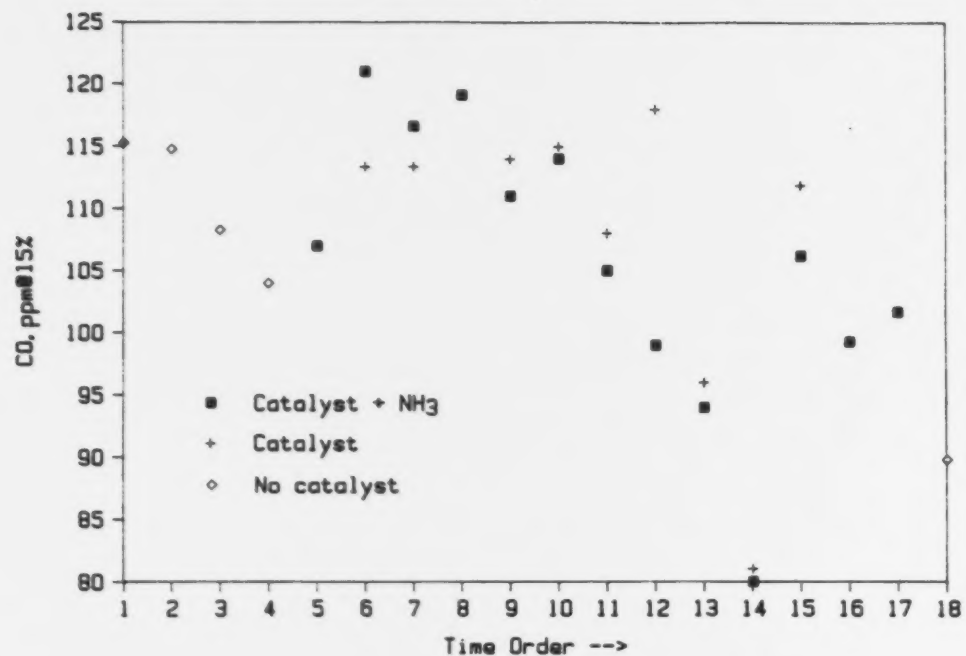


Figure 3. CO emissions, diesel catalyst tests.

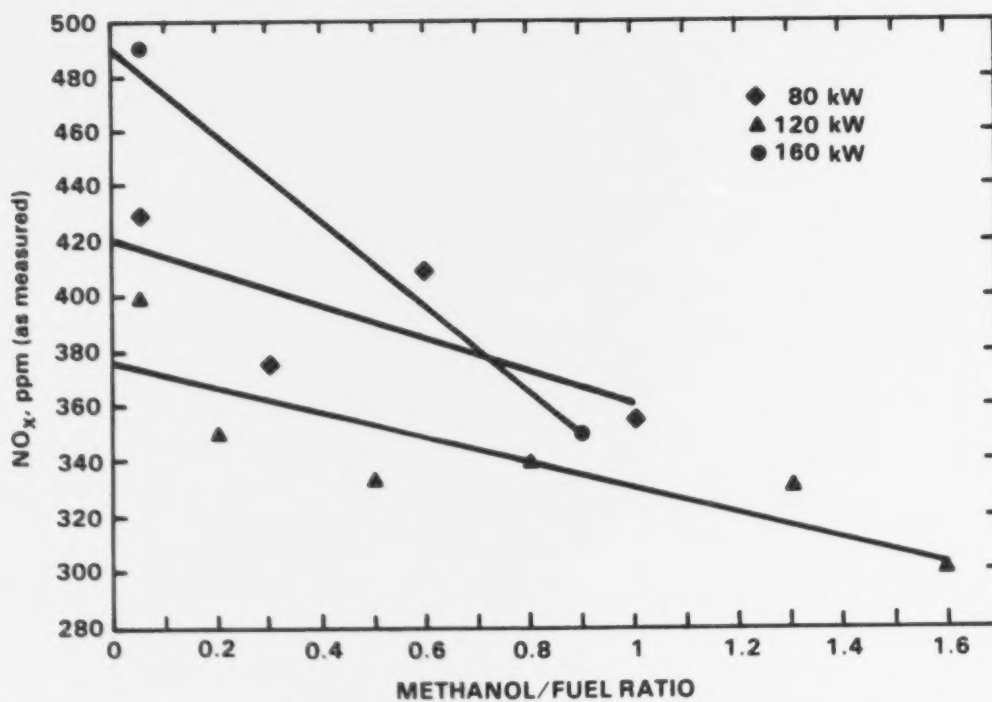


Figure 4. Effect of methanol and load on NO_x emissions.

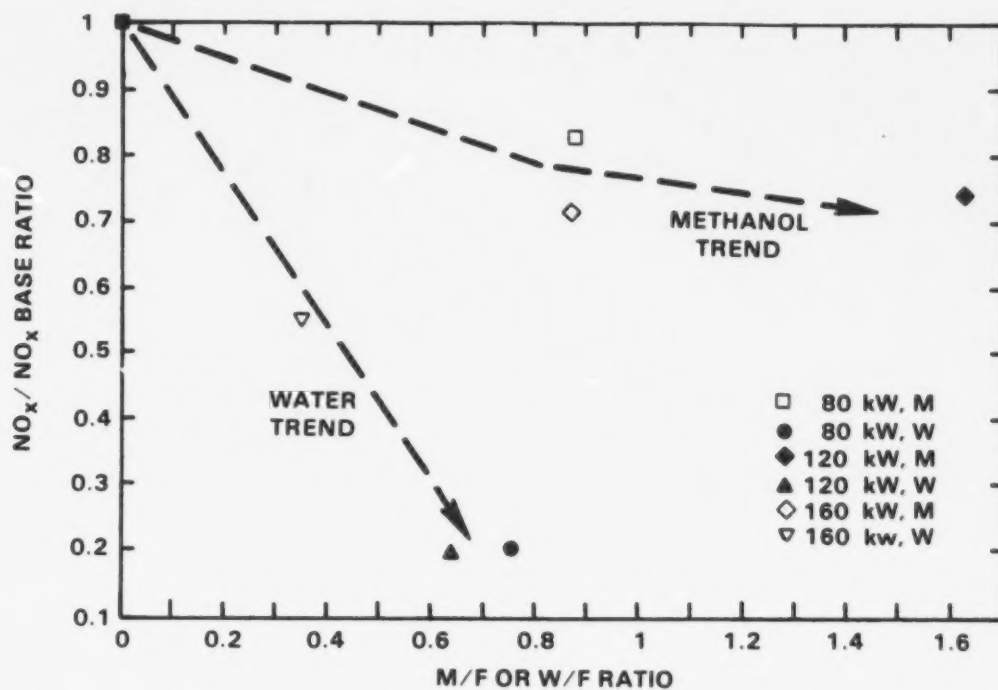


Figure 5. Effect of methanol and water on NO_x emissions.

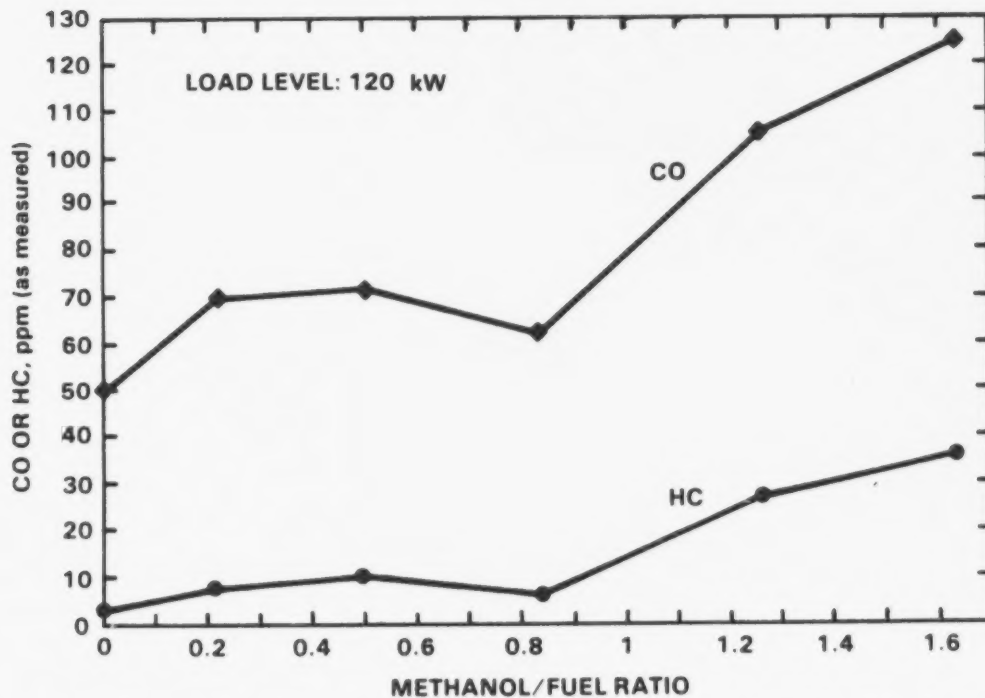


Figure 6. Effect of methanol on CO and HC emissions (120 kW).

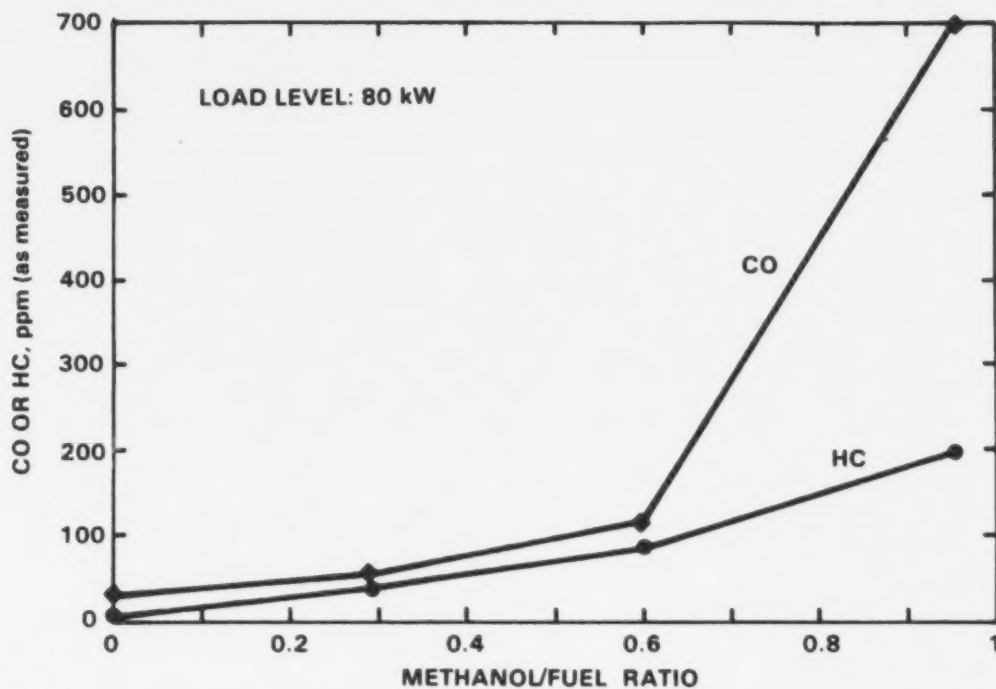


Figure 7. Effect of methanol on CO and HC emissions (80 kW).

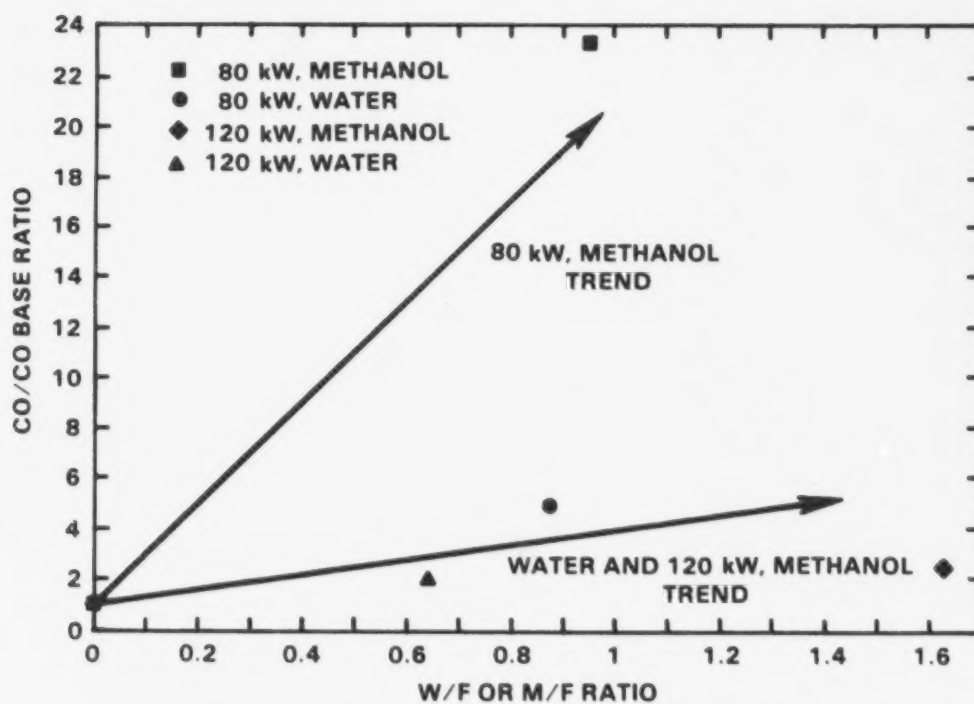


Figure 8. Effect of methanol and water on CO emissions.

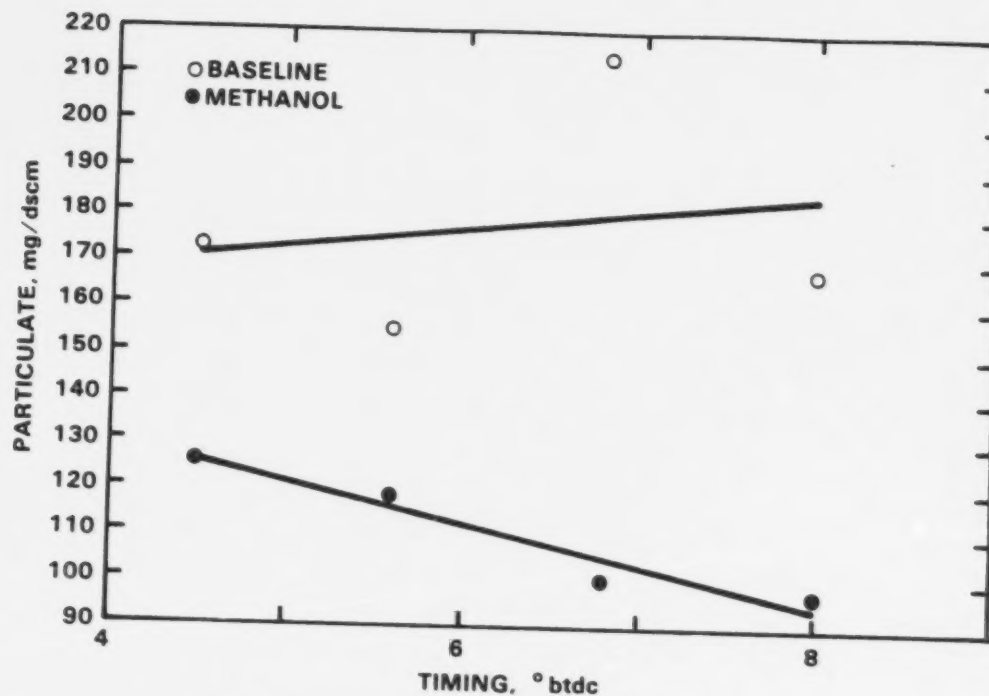


Figure 9. Particulate emissions variation.

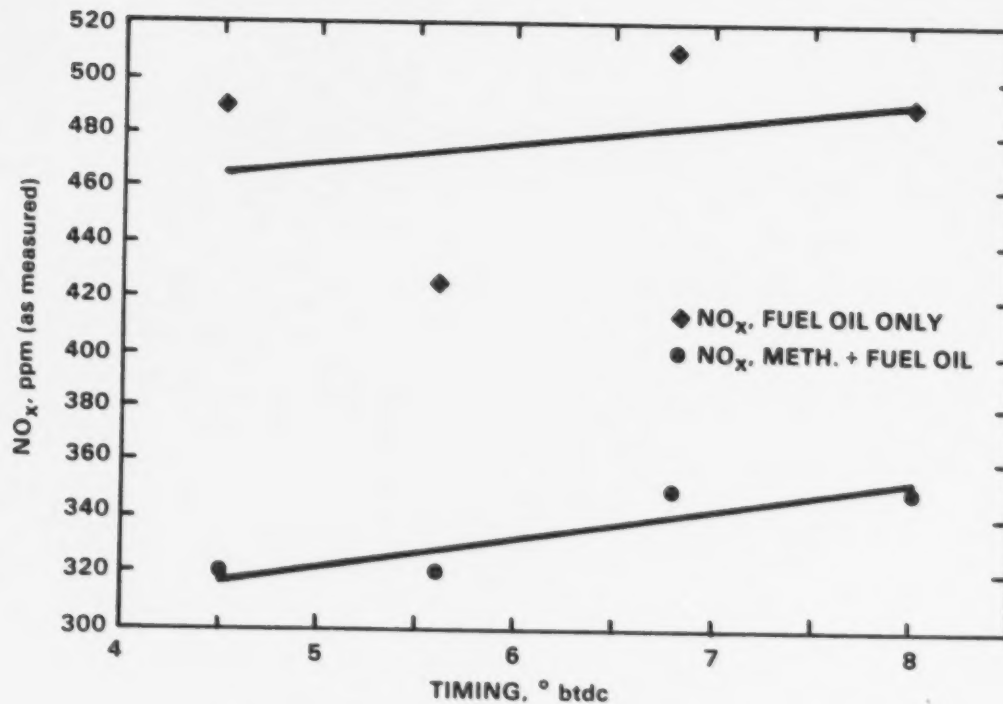


Figure 10. NO_x emissions variation.

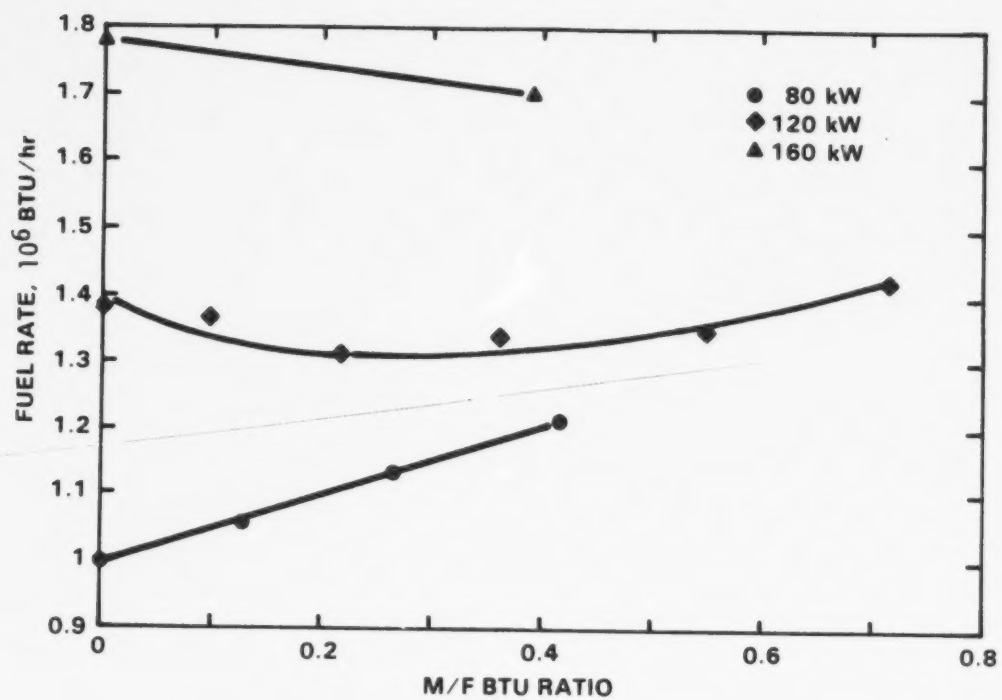


Figure 11. Effect of methanol on energy consumption.

TABLE 1: NO_x DATA
Diesel Catalyst Life Test
(NH₃/NO_x Ratio Range 1.0 to 1.1)

Date	Hours	% NO _x Reduct.	NO _x (ppm)	Event:
-----	-----	-----	-----	-----
Se13-84	7	96.8	12.5	First day of catalyst testing
Se18-84	13	95.7	18.5	
Se21-84	22	97.8	9.0	
Se24-84	26	97.7	9.0	
Se25-84	34	96.6	13.0	
Se27-84	50	97.0	13.0	
Oc01-84	54	96.9	13.0	
Oc16-84	235	97.1	11.0	
Oc29-84	438	95.0	19.0	
No05-84	540	91.1	35.0	
De13-84	1031	92.3	27.0	After first catalyst cleaning
De17-84	1063	92.3	30.0	
Ja15-85	1242	87.5	50.0	
Ja22-85	1321	86.4	55.0	
Fe14-85	1652	83.2	68.0	
Mr14-85	1955	69.1	108.0	
Mr19-85	1983	74.3	95.0	
Mr19-85	1985	85.0	60.0	
Mr20-85	2007	80.3	70.0	
Mr25-85	2055	78.8	68.0	
Mr28-85	2110	79.1	70.0	After second cat. cleaning
Ap12-85	2263	83.1	65.0	
Je06-85	2969	77.6	75.0	
Jy31-85	3366	85.5	47.0	
Au01-85	3390	84.2	52.0	
Au05-85	3396	86.9	51.0	
Au27-85	3600	85.5	50.0	
Se03-85	3647	77.9	74.0	
No05-85	3884	78.3	100.0	
De04-85	3896	87.6	55.0	After third catalyst cleaning
De05-85	3908	90.2	45.0	
De05-85	3916	91.8	40.0	
De18-85	3921	87.9	57.0	
De19-85	3933	85.4	65.0	
Ja07-86	3950	84.0	70.0	
				Final catalyst test

TABLE 2: CO DATA TABLE
Diesel Catalyst Life Test

Test No.	Catalyst + NH ₃ CO(ppm,15%)	Catalyst CO(ppm,15%)	No Catalyst CO(ppm,15%)	Date
1			115.3	Jy03-84
2			114.8	Jy23-84
3			108.3	Jy25-84
4			104.0	Jy30-84
5	107.0			Se25-84
6	121.0	113.4		Oct10-84
7	116.6	113.4		Nov05-84
8	119.1			Dec13-84
9	111.0	114.0		Dec17-84
10	114.0	115.0		Mar13-85
11	105.0	108.0		Mar14-85
12	99.0	118.0		Mar20-85
13	94.0	96.0		Apr12-85
14	80.0	81.0		Jun06-85
15	106.2	111.9		Dec19-85
16	99.3			Jan06-86
17	101.7	101.8		Jan07-86
18			89.8	Jan09-86
Avg.	105.68	107.25	106.44	

TABLE 3: METHANOL TEST DATA

Load (kW)	Fuel oil (Lph)	Methanol (Lph)	NO _x (ppm)	CO (ppm)	HC (ppm)	Oxygen (%)
80	27.3	0.0	430	30	4.0	12.08
"	25.7	7.6	375	55	39.5	11.97
"	24.6	14.8	410	120	87.0	11.76
"	23.5	22.3	355	700	200.0	11.03
120	37.9	0.0	400	50	2.5	10.71
"	34.1	7.6	350	70	7.5	10.71
"	29.5	14.8	333	72	10.0	10.71
"	26.9	22.3	340	62	6.0	10.71
"	23.8	29.9	330	105	27.0	10.50
"	22.7	37.1	300	125	36.0	10.50
160	48.8	0.0	490	25	2.0	9.98
"	33.6	30.0	350	28	3.0	9.98

TABLE 4: TIMING DATA @ 160 kW

Timing (°btdc)	Part.b (mg/scm)	Part.m (mg/scm)	Fuelbase (Lph)	Fueltot (Lph)	Fueloil (Lph)	NO _x base (ppm)	NO _x meth (ppm)
4.5	172.69	125.76	52.23	30.00	37.75	490	320
5.6	154.86	118.39	49.96	30.00	36.62	425	320
6.8	214.56	99.82	49.2	30.00	33.96	510	350
8	167.96	96.66	48.83	30.00	33.59	490	350

TABLE 5: FUEL EFFICIENCY DATA

Load (kW)	Fueloil (Btu/hr)	Methanol (Btu/hr)	Total (Btu/hr)
80	996668	0	996668
"	938256	121197	1059453
"	898097	236016	1134113
"	857938	355618	1213556
120	1383653	0	1383653
"	1244923	121197	1366120
"	1076986	236016	1313002
"	982065	355618	1337683
"	868890	476815	1345705
"	828732	591634	1420366
160	1781590	0	1781590
"	1226669	478410	1705079

THE CONTROL OF NO_x EMISSIONS FROM
MUNICIPAL SOLID WASTE INCINERATORS

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ABSTRACT

The disposal of Municipal Solid Waste is a growing problem because of the declining capacity of landfills and restrictions on their use. Incineration provides a cost effective solution; the bulk of material requiring landfilling is reduced, the material can be landfilled with minimal restrictions, and the energy in the waste is converted to usable heat and/or power. Incineration cannot be accomplished without due consideration to the generation and control of atmospheric pollutants. Of major concern are trace quantities of potentially toxic hydrocarbons. The emission of these species can be minimized by appropriate design and operation of the combustion system, unfortunately these measures tend to increase rather than decrease emissions of nitrogen oxides. This paper will discuss the types of municipal waste combustion devices and the types of pollutants generated during waste combustion. Four methods of NO_x control are discussed: a) Combustion Zone Control; b) Selective Non-Catalytic; c) Selective Catalytic; and d) Hybrid Processes.

INTRODUCTION

Currently, many U.S. municipalities are confronted with major problems in the disposal of solid waste. Faced with declining landfill capacity, state and local governments have turned to solid waste management plans which will reduce landfilling requirements. A critical component of those plans is the use of combustion to reduce the volume of material that must be landfilled and, at the same time, generate usable energy and electrical power. Approximately 60 percent of the solid waste generated by municipalities could be combusted and a small additional portion could be recycled. Residue from municipal solid waste (MSW) incineration facilities and that portion of MSW which cannot be incinerated or recycled must still be landfilled. However, the potential for simultaneously reducing the volume of waste to be landfilled and generating steam or electric

power is often of great economic benefit to municipalities. For this reason, a large number of municipalities are currently considering waste-to-energy projects. It is expected that the number of waste-to-energy plants within the United States will dramatically increase in the next decade. Some estimates indicate that the amount of waste being burned will increase by a factor of three by 1990 with a further doubling by the 21st century.

MSW, unlike fossil fuels, is extremely heterogeneous. Its composition varies with the seasons and is affected by weather; thus, its calorific value can vary widely and many systems are therefore designed to handle wastes with heating values ranging from 3,800 to 5,200 Btu/lb. The size of MSW also varies and this affects the ability to feed the material to the combustion device. There are three major classes of MSW incinerators and these differences in their design philosophies make them more or less tolerant to variations in fuel input properties which are imposed by the characteristics of MSW. The three incinerator types are:

- Mass burning excess air (mass burn)
- Starved air two stage (modular)
- Refuse derived fuel firing (RDF)

RDF can be burned in fluidized bed incinerators, but they represent only a small fraction of the waste-to-energy systems either in service or planned.

MASS BURN

Figure 1 presents an example of the major features of a modern mass burning facility including:

- Waste storage, handling and feeding system (1,2,3)
- Combustion systems (4,5)
- Boiler and generators (6,11)
- Air pollution control equipment (7,9,10)
- Residuals handling (13,13,14)

The major distinguishing features of mass burn technologies is the lack of virtually any processing of the refuse and the large capacities (>100 TPD). The combustion systems consist generally of a grate on which the solid waste burns in a layered bed that is progressively moved down the grate. The air required for combustion of the waste is introduced both underneath the grate and directed through the bed (referred to as primary air) and above the bed through secondary air jets.

STARVED AIR TECHNOLOGIES

The term "modular incinerator" implies that the unit is constructed at the manufacturer's facility and shipped as a module(s) to the installation site. Initial development of this type of MSW system came as an advancement to the small batch-fed incinerators used to burn waste from hospitals, stores, restaurants, etc. The first facility to combine a capability for continuous operation and energy recovery was installed in 1976 by Consumat Systems, Inc. in North Little Rock, Arkansas.

Figure 2 illustrates the basic components of starved-air systems which are typically small (less than 100 ton/day capacity per unit). MSW is generally fed to the system with a front-end loader and charged into the primary chamber with a hydraulic ram. The typical solids residence time in the first stage chamber is on the order of 10 to 12 hours which helps to damp out variations in fuel heating value and the discrete nature of the charging process. The primary zone functions as a gasifier with only about 40 percent of the theoretical air requirements. The relatively large volume of this chamber coupled with low air flow results in low gas velocity and minimal particulate entrainment.

REFUSE DERIVED FUEL

As discussed earlier, MSW is a heterogeneous, highly variable fuel and there are two basic approaches to dealing with this problem of variability. The mass burn and starved-air systems accept the variability of MSW as a fuel characteristic to be controlled in the combustion system design. The alternate approach is to pre-process MSW to generate a more uniform fuel. The objective is to modify the fuel characteristics sufficiently for the refuse-derived fuel (RDF) to be burned in boilers designed for fossil fuels, e.g. spreader stoker and suspension fired units. Also, RDF might be burned in cyclone boilers, pulverized coal-fired boilers or fluidized bed furnaces. Processed fuel might be burned separately or it might be burned in a cofiring configuration using the RDF as a supplement to the baseline fossil fuel.

The development of extensive waste-to-energy systems is not without a panacea for all environmental problems. One major concern that stems from proliferation of waste-to-energy plants is trace emissions of potentially toxic organic compounds. Of particular concern (and intense public interest) are the isomers of dioxin and furan species, with major concern centering on 2,3,7,8 Tetrachlorodibenzo-p-dioxin (TCDD). MSW contains metals, chlorine, sulfur and nitrogen and a normal efficient combustion system will generate particulate and gases which are considered pollutants. In addition, the extreme variability of the fuel can give rise to poor combustion and the generation of partial combustion products such as hydrocarbons, carbon monoxide and carbonaceous particulate. This paper will consider the mechanisms controlling the emission of these various pollutants from MSW combustors and the impact of design features on the formulation of potentially toxic hydrocarbons which will also impact NO_x emissions. Finally, the paper will address NO_x emission and control from MSW combustors.

ORGANIC EMISSIONS FROM MSW COMBUSTORS

The combustion of MSW can result in a number of pollutant species in addition to nitrogen oxides, including:

- Potentially toxic trace organics
- Carbon monoxides
- Particulate matter both carbonaceous and fine particulate containing metals (As, Be, Cl, Pb, Hg, Ni)
- Acid gases (HCl , SO_2 , HF , H_2SO_4)

Some of the pollutants are present in the effluent because of the composition of the waste (metal containing particulate and acid gases) or because of inefficiencies in the combustion process (organics and carbon monoxide). Public

concern centers around the emission of trace organic species because of the perceived health threat.

MECHANISMS OF FORMATION

There are a number of potentially toxic organic compounds that have been identified in the effluent from MSW incinerators. At present, the principle emphasis is being placed on the chlorinated isomers of dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF). However, PCDD and PCDF comprise only one of many types of organics emitted from MSW incinerator facilities that may be of concern eventually.

There are many different theories concerning the formation of PCDDs and PCDFs from MSW combustion systems (Germanus, 1985; Niessen et al. 1984, 1986). The best-supported theories are illustrated in Figure 3. The first theory involves the breakthrough of unreacted PCDD/PCDF present in the raw refuse. A few measurements have indicated the presence of trace quantities of PCDD/PCDF in the refuse feed but in order to account for the measured exhaust levels, none of this material could have reacted during combustion which is unlikely (Germanus, 1985).

A more plausible theory involves the conversion of species referred to as precursors which have similar structure to the organic species of concern. For example, relatively simple abstraction and combination reactions can convert chlorophenols and polychlorinated biphenyls to PCDD/PCDFs. These precursors can be present in significant quantities in the refuse and, in addition, can be produced by pyrolysis in oxygen-starved zones. There is direct evidence of gas phase yields of PCDD/PCDF from PCB fires (Axelrod, 1985) and lab and bench-scale studies on PCB, chlorinated benzene and chlorinated phenols (Olie et al. 1983; Hutzinger et al. 1985).

The third mechanism illustrated in Figure 3 involves the synthesis of PCDD/PCDF from a variety of organics and a chlorine donor. Again, the simplest mechanisms involve those species that are structurally related to PCDD/PCDF but a full spectrum of plausible combustion intermediate chemistry could be proposed to lead to precursors and eventually to PCDD/PCDFs. For example, the analysis for intermediates formed during the combustion of complex fuels such as coal and wood indicate yields of (unchlorinated) dioxin and furan species (Hites and Howard, 1978) that could be chlorinated when a suitable chlorine donor is available. Complex fuels which contain lignin have been shown to yield higher levels of PCDD/PCDF than non-lignin fuels (Niessen, 1984).

The final hypothetical mechanism involves catalyzed reactions on fly ash particles at low temperatures. The lab scale evidence indicates that the chlorination of related-structure precursors on fly ash particles to form PCDD/PCDF can occur but that the rates are relatively slow (Eiceman et al. 1982; Rhgei et al. 1982).

In summary, current theories on the formation of PCDD/PCDF involve either unburned PCDD/PCDF from the refuse or related-structure precursors, or precursors that are likely to be formed in oxygen-starved zones of the furnace. The precursors can be converted to PCDD/PCDF even at low temperatures on fly ash. Hence, it is important to destroy the PCDD/PCDF and the precursors in the furnace. Therefore, the destruction mechanisms are equally as important as the formation mechanisms. Assuring complete destruction will likely be the more appropriate combustion control method rather than the prevention of formation.

The destruction of PCDD/PCDF is expected to be similar to the oxidation of other aromatic chlorinated hydrocarbons primarily involving free radicals (such as OH) which attack the structure or unimolecular decomposition (Shaub and Tsang,

1983). The details of the mechanism are uncertain and more fundamental research is required. Direct experimental measurements of the thermal decomposition characteristics of non-chlorinated dioxin and furan species are available from data at the University of Dayton Research Institute (UDRI) (Duvall and Rubey, 1977). These studies using the Thermal Decomposition Analytical System (TDAS) provide a definition of the thermal requirements for destruction under highly diluted reactant conditions. These condition, sometimes referred to as non-flame, provide a conservative indication of the temperature to which the test species must be subjected in order to achieve destruction.

The thermal decomposition data indicate that relatively low temperatures are required to destroy dioxin and furan and that the temperature requirements are similar to the decomposition temperature required for non-substituted biphenyl. Chlorinated biphenyls have higher decomposition temperatures and a similar increase in the temperature requirements are expected for PCDD/PCDF due to the expected similarity of the decomposition mechanisms of PCB and PCDD/PCDF. These data indicate that 800°C (~1500°F) is a characteristic temperature for high levels of destruction (>99.9 percent) of PCB and by analogy for destruction of PCDD/PCDF. This temperature is in general agreement with the Dow Chemical conclusions that TCDD decomposition occurs above 800°C (Bumb, et al. 1980, Stehl et al. 1973). Other potential precursors to the formation of PCDD/PCDF can have somewhat higher decomposition temperatures but are still low relative to combustion temperatures. The UDRI decomposition data (Rubey et al. 1983 and Dellinger et al. 1983) also indicates that temperature is more important than residence time. Effective combustion control schemes must ensure that all PCDD/PCDF and precursors experience the required threshold temperature if they are to be destroyed. For PCDD/PCDF and potential precursors, the threshold temperature is near 1700°F (925°C).

Another possible control scheme involves removal of PCDD/PCDF from the flue gas. PCDD/PCDF are condensible at flue gas temperatures and will deposit on fly ash particles very efficiently. The condensation will occur preferentially on smaller particles because of the higher surface areas of smaller particles. Hence, a removal system must efficiently remove the finer particles in order to effectively remove PCDD/PCDF. Data on full scale tests have clearly shown the effectiveness of a high efficiency baghouse with dry injection flue gas treatment (Martin, 1986) in removing PCDD/PCDF from the flue gas.

COMBUSTION CONTROL TRACE ORGANIC EMISSIONS

Thermodynamic equilibrium considerations indicate that under excess air conditions and the characteristic temperatures typical of incinerators, emissions of organic species should be so low that they can be considered to be zero. However, measurements have been made showing significant emissions of trace organic species some of which are toxic. The basis for combustion control of emissions of organics from MSW incinerators is to provide conditions whereby the combustion products can approach equilibrium. This requires that all combustion products are effectively mixed with oxygen at a temperature which is sufficiently high to allow the rapid destruction of all organic species. Table 1 illustrates the wide variability in dioxin and furan emissions from various facilities from which field test data is available. The emission rate for total dioxins and total furans vary by four to five orders of magnitude. Data forming the high end of the emission rate come from field tests performed on the facility at Hampton, Virginia (Haile, 1984; Scott Environmental Services, 1985; Nunn, 1983; Howes, 1982) and at Philadelphia, Northwest (Neulicht, 1985). Both of these facilities represent older designs where the primary design concern was waste volume reduction. Data forming the low end of the emission range come from field tests performed on new facilities at Tulsa, Oklahoma (Seelinger, 1986), at Marion County, Oregon (Ogden Projects, 1986) and at the Westchester facility at Peekskill, New York (New York State

Department of Environmental Conservation, 1986). Each of these new facilities' designs is based on extensive research and development efforts by the manufacturer to produce MSW incinerator systems with high thermal efficiency and low trace organic emission rates.

Thus, it appears that combustor design has a major influence of the emission of trace organic species from MSW incinerators. Modern designs probably achieve these emission rates by:

1. Limiting the formation of both PCDD/PCDF and their precursors.
2. Maximize the destruction of these components prior to the combustor boiler exit.

As such, good combustor design practice attempts to preclude conditions which promote the formation of PCDD/PCDF, their precursors and to ensure that the environment experienced by the gaseous products of waste combustion will destroy both dioxins and dioxin precursors if those compounds have been formed. These conditions are:

- Mixing of fuel and air to prevent the existence of long-lived fuel-rich pockets of combustion products
- Sufficiently high temperatures in the presence of oxygen for the destruction of hydrocarbon species
- Prevention of quench zones or low temperature pathways that would allow partially-reacted fuel (solid or gaseous) from exiting the combustion chamber.

Efficient mixing and high temperatures minimize the emissions of trace organic species but they increase the tendency for the combustor to produce nitrogen oxides (NO_x).

NO_x FORMATION DURING MSW COMBUSTION

Air emissions of NO_x from MSW incinerators are highly variable. Measurements have been made on a number of plants as summarized by O'Connell et al. (1982), Rigo et al. (1982), Russel and Roberts (1984) and MRI (1986). Discussions with manufacturers have further indicate the high variability of NO_x emissions. The reported levels range from less than 0.05 to near 1.0 lb/MMBtu with average values for all facilities reported at around 0.25 lb/MMBtu (130 ppm at 12 percent CO_2). The sources have indicated that there is no clear trend in NO_x emissions from different types of MSW incinerators.

The NO_x formed in MSW combustion facilities occurs by two separate pathways, thermal fixation of molecular nitrogen ("thermal NO") and conversion of nitrogen from the fuel ("fuel NO"). The thermal fixation mechanism involves high temperature reactions of free radicals of molecular nitrogen and oxide. As illustrated in Figure 4, thermal NO formation is extremely sensitive to temperature which is not the case with fuel NO. As shown in Figure 4, fuel NO formation is almost insensitive to temperature. Comparison of actual emissions with the calculations shown in Figure 4 suggest that: 1) fuel nitrogen could be a significant source of NO and 2) the local conditions under which NO is formed are not characterized by a well mixed adiabatic temperature. Figure 4 implies that fuel nitrogen conversion accounts for less than 100 ppm NO_x even for fuels containing 0.5 percent by weight of nitrogen. Nitrogen free fuel would have

emissions on the order of 10 ppm. In mass burn systems the fuel may be predicted as it passes along the bed which may be slightly oxygen rich. Therefore, local temperatures close to the bed will probably exceed the adiabatic temperature range shown in Figure 4 which will account for levels of NO in excess of 100 ppm. The problem associated with MSW combustor design and NO_x control is simply that conditions which tend to minimize the formation and emissions of trace organic species will maximize the formation of nitrogen oxides.

CONTROL OPTIONS FOR NITROGEN OXIDES

Figure 5 presents schematics of four major classes of NO_x control schemes that have been applied or are planned to be tested for the control of NO_x emissions from MSW combustors.

COMBUSTION ZONE CONTROL (FIGURE 5a).

Two options are available to control NO_x emissions in the combustion zone. First, flue gas recirculation prevents NO_x formation and second, reburning destroys NO that is formed in the bed.

Flue gas recirculation (FGR) is a demonstrated technology for the control of thermal NO in boilers. FGR acts as a thermal diluent and reduces combustion temperatures. This scheme has been demonstrated by manufacturers as an effective means of controlling NO_x in its refractory-lined high temperature incinerators. Flue gas recirculation lowers flame and furnace temperatures which could be counter to the control of PCDD/PCDF. The significance of the detrimental impact on PCDD/PCDF emissions due to reduced bulk temperatures has yet to be determined. Testing recently completed on the Pittsfield incinerator by the State of New York could provide information addressing the impacts of FGR when they become available.

Reburning is a term used for a control technique which involves the use of a hydrocarbon containing fuel as a reducing agent. Hydrocarbon radicals react with NO forming nitrogen containing radicals which form N₂ by reaction with NO in the absence of oxygen. This control technology is being developed for use in fossil fuel fired boilers because only minor modifications are required to the main heat release zone. Thus, with reburning the main heat release zone can be optimized for efficient combustion, eliminating problems due to slagging, corrosion and flame impingement. The effectiveness of reburning for NO control has been shown to be a function of:

- Initial NO level; the formation reduction decreases as the initial NO level decreases,
- Fuel type; nitrogen free reburning fuels are most effective, particularly at low initial NO levels,
- Stoichiometry; reburning is most effective if the stoichiometry of the reburning zone is reduced to approximately 90 percent of the theoretical air requirement in the primary combustion zone. Thus, the amount of reburning fuel for optimum reburning effectiveness is dependent on the level of excess air.
- Temperature, reburning effectiveness increases as the temperature of reburning zone increases;
- Residence times in the reburning zone of approximately 0.5 seconds are required to maximize the effectiveness of reburning.

The conditions within a MSW combustor are not ideal for traditional reburning approaches since the unit operates at relatively low temperatures and high excess air levels. However, since moderate levels of control are necessary, reburning with natural gas could be a cost effective control technique particularly as there could be a reduction in the emission of trace organic species due to the increased heat release and radical concentrations above the bed. Reburning may be designed into new units for optimized NO_x control and for simultaneous control of trace organics.

SELECTIVE NON-CATALYTIC NO REDUCTION (FIGURE 5b)

These approaches are generally effective over a relatively narrow range of injection temperatures. Since temporal and spatial variations in temperature and stoichiometry are inherent in MSW incineration, the efficiency of any selective non-catalytic technology that depends on fine tuning of the injection temperature is bound to suffer. Several selective reagents have been used or proposed.

DE-NO_x (NH₃ ADDITION)

Thermal de-NO_x (Lyon) involves the injection of NH₃ into post-flame combustion gas. The chemistry is at least grossly understood to be as follows:



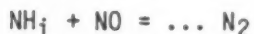
The NO reduction occurs over a relatively narrow temperature window between 1600 and 1850°F. At higher temperatures the added NH₃ is efficiently oxidized to NO, while at lower temperatures there are insufficient flame radical concentrations to initiate the NH₃ reaction.

UREA

The injection of urea has also been found to reduce NO_x in post-flame gases. The exact chemistry has not been defined to the same degree as that for de-NO_x. However, it is anticipated that the decomposition of the urea produces a reduced nitrogen species that reacts directly with NO to produce N₂. Use of urea has the advantage that it may be stored and injected into the furnace as a liquid through strategically located spray nozzle.

CYANURIC ACID

Recent fundamental chemistry work has discovered that the addition of cyanuric acid to combustion effluents causes a reduction in NO (Perry and Siebers, 1986). The indicated temperature for efficient reduction is about 1050-1200°F. The reaction chemistry has not yet been defined, although the following steps have been proposed:



EMCOTEK

In this proprietary process an unspecified reagent is added to the post-flame gas to promote conversion of NO to NO₂. The practical application of MSW incineration is that if a scrubber is needed to remove HCl, then NO₂ may also be wet scrubbed with little additional effort or cost.

SELECTIVE CATALYTIC REDUCTION (FIGURE 5c)

The use of selective catalytic reduction techniques (SCR) is being actively pursued in Germany for the control of NO_x conversion from coal fired boilers. Application to MSW combustors may be difficult because of variability in exhaust gas composition, the potential for catalyst poisoning as well as high overall system cost.

HYBRID PROCESSES (FIGURE 5d)

A "Hybrid Process" refers to a combination of techniques to maximize the reduction at the optimum cost. Reburning could be applied with selective non-catalytic reduction or two reduction reagents could be used in different temperature windows to take advantage of the best features of each process.

CONCLUSIONS

Over the past several years there have been numerous advancements in technology and hardware used for incineration of municipal solid waste. Modern facilities should be viewed as large steam generating facilities using solid waste as a fuel rather than a thermal garbage disposal. During that period, system designers have learned to overcome corrosion problems, fuel handling problems, reliability problems and in the process designs have evolved which significantly reduce emissions of potentially toxic trace organics. Unfortunately, those system conditions appear to be ideal for increasing NO_x conditions.

Several state regulatory groups are actively incorporating NO_x emission limits into the operating permits for new MSW incinerators. The current paper has briefly outlined several of the NO_x control approaches which may be adapted to MSW systems. Units in both Europe and the United States have successfully applied FGR for NO_x control. Recent testing of a facility in New York should provide an indication of the extent of tradeoff between NO_x and dioxin emissions. Data should also be available shortly on the efficiency of MSW incinerator NO_x control using the Exxon thermal de- NO_x process.

Other NO_x control approaches using reburning, selective non-catalytic reduction, selective catalytic reduction as well as hybrid approaches may be possible but have not yet been demonstrated. The reburning process and/or the hybrid processes have the potential for simultaneously controlling NO_x and trace organic emission. It is important, however, to recognize that successful development of these technologies will require a significant amount of R&D as well as careful integration of the controls into the overall MSW combustion system. Design of MSW incinerators as an overall system has allowed many of the previous operational and trace organic emission problems to be effectively solved. That same approach can be effective for NO_x control as well.

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Pollutant	Emission Concentration Range ^a		
	Mass Burn	Starved Air	RDF-Fired
2,3,7,8 TCDD ^b	0.019-62.5	1.54 ^c	0.522-14.6
2,3,7,8 TCDF ^d	0.168-448	-- ^e	2.69 ^c
TCDD ^f	0.195-1,160	1.22-19.1	3.47-258
TCDF ^g	0.322-4,560	14.7-124	31.7-1,680
PCDD ^h	1.13-10,700	75.9-227	64.4-4,300
PCDF ⁱ	0.423-14,800	116-250	96.2-8,100

a Concentrations expressed in ng/Nm³ at 12% CO₂

b 2,3,7,8 Tetrachlorodibenzo-p-dioxin

c Data available for only one test

d 2,3,7,8 Tetrachlorodibenzofuran

e No data available

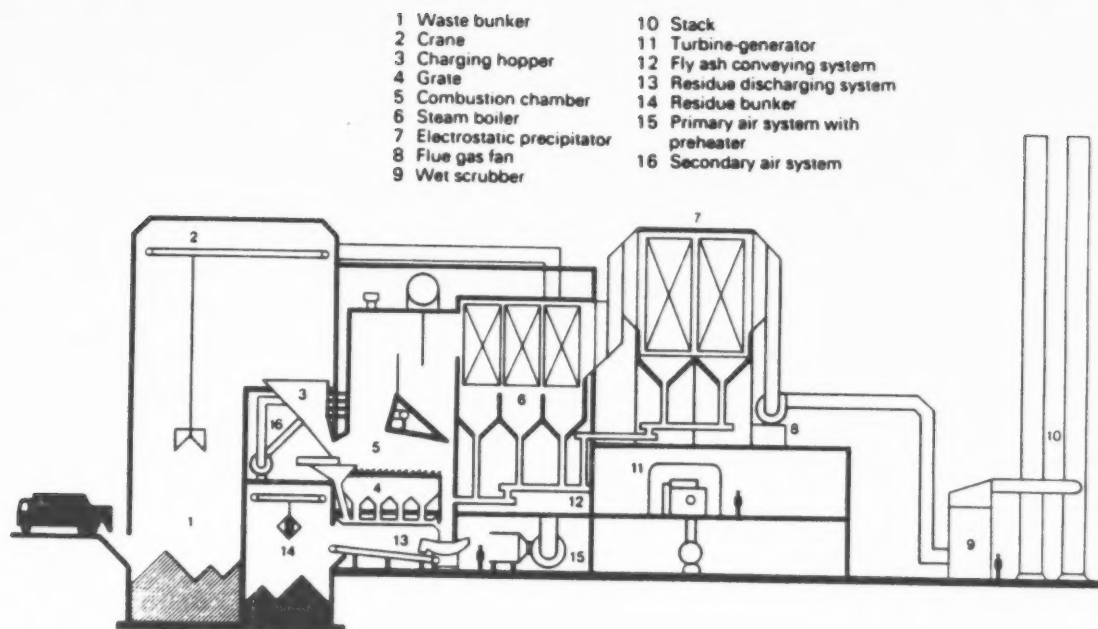
f Tetrachlorodibenzo-p-dioxin

g Tetrachlorodibenzofuran

h Polychlorinated dibenzo-p-dioxin

i Polychlorinated dibenzofuran

Table 1. Summary of Organic Emission Ranges From Full-Scale MSW Facilities



Longitudinal section of the
Waste power plant Bielefeld-Hertford,
Federal Republic of Germany
Combustion capacity: $3 \times 385 \text{ t/24 h}$
Steam production: $3 \times 52.4 \text{ t/h}$

Figure 1. Mass Burning Waste Power Plant Designed by
Widmer and Ernst at Bielefeld-Hertford,
Germany

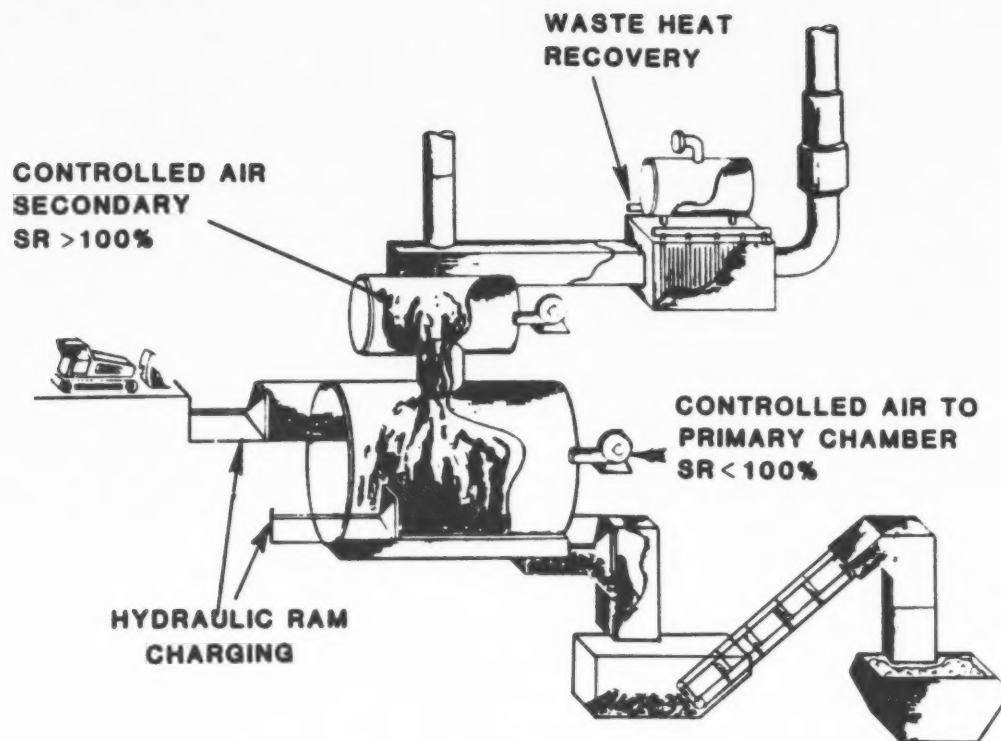
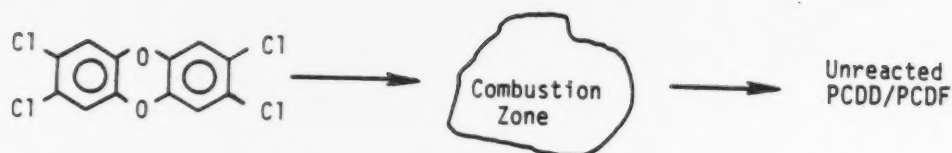


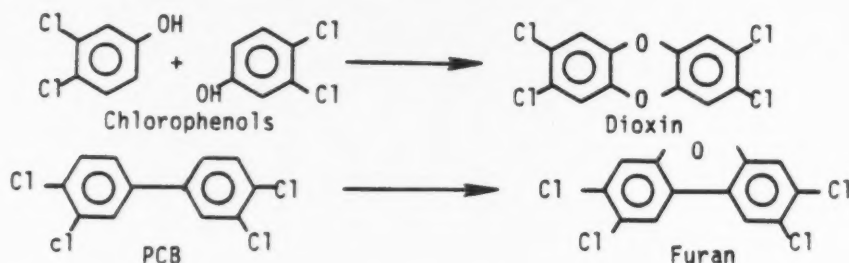
Figure 2. Components of Typical Starved-Air Modular Incinerator

I. DIOXIN IN REFUSE



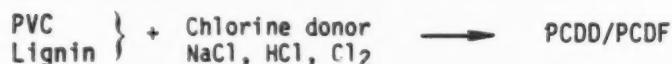
Evidence: Occasional PCDD/PCDF contamination in refuse

II. FORMATION FROM RELATED CHLORINATED PRECURSORS



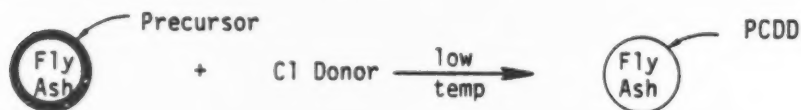
Evidence: PCDD/PCDF on soot from PCB tires
Lab and bench studies of PCB, Chlorinated Benzene and Chlorinated Phenols yielded PCDD/PCDF

III. FORMATION FROM ORGANICS AND CHLORINE DONOR



Evidence: Lab scale tests of vegetable matter, wood, lignin, coal with chlorine source yielded PCDD/PCDF

IV. SOLID PHASE FLY ASH REACTION



Evidence: Lab scale demonstrating potential for ash catalysis reactions of PCDD's to other homologues.

Figure 3. Hypothetical Mechanisms of Dioxin Formation Chemistry

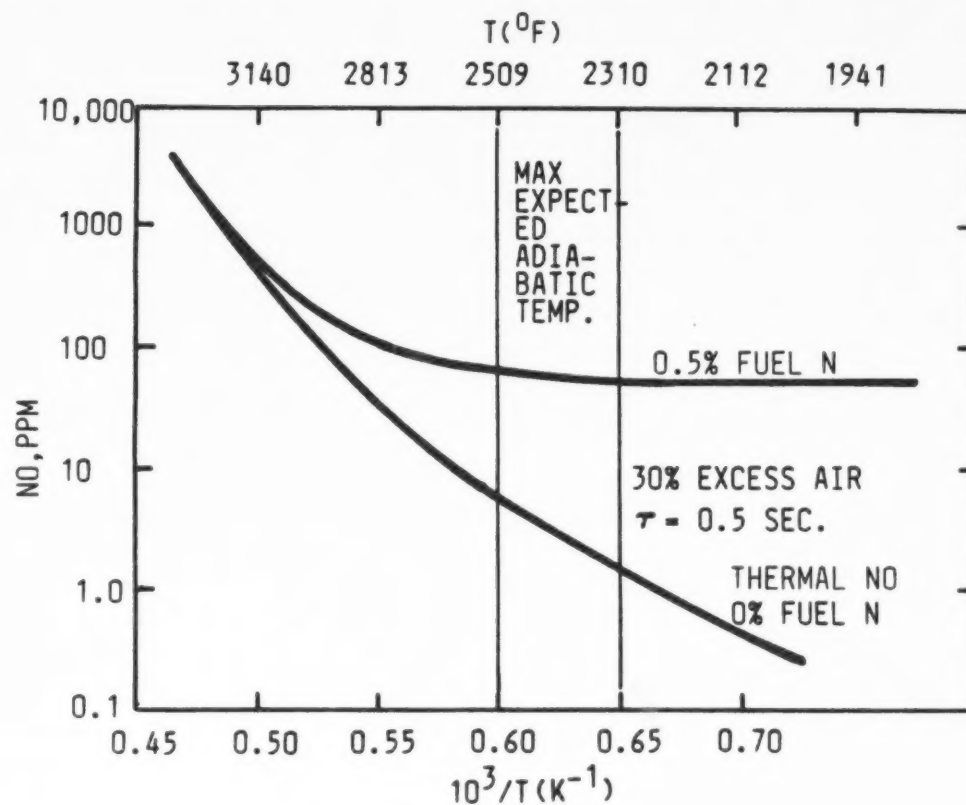
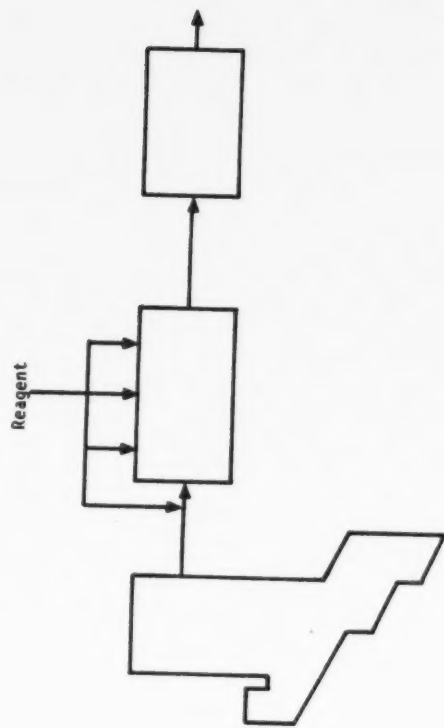
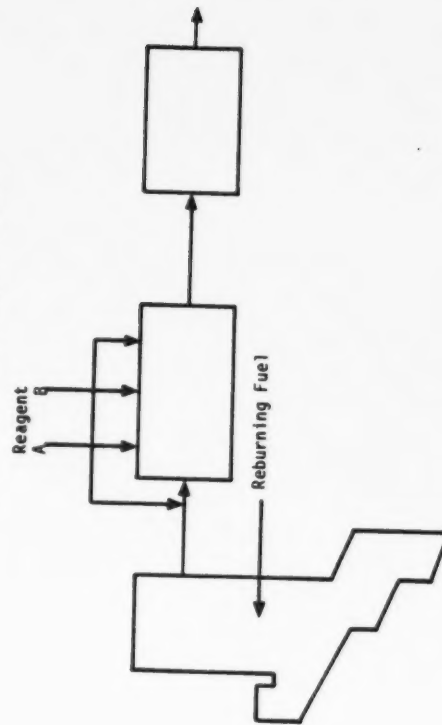


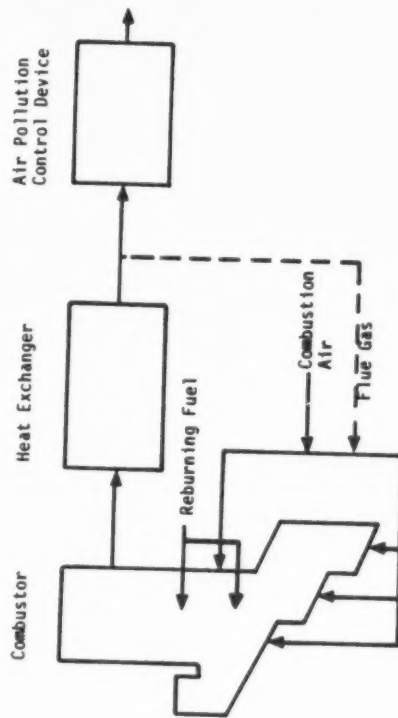
Figure 4. Impact of Temperature and Fuel Nitrogen on NO_x Emissions for Excess Air Conditions (Calculated Using EER Kinetic Set)



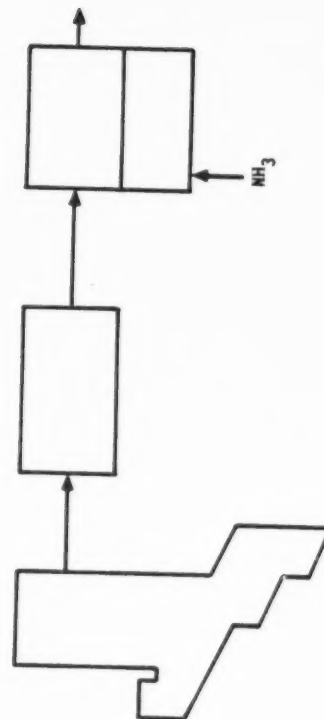
b) Selective Non-Catalytic Removal



d) Hybrid Control Processes
 i) Reburning + A or B
 ii) A + B



a) Combustion Zone Control



c) Selective Catalytic Removal

Figure 5. Schematic of Various NO_x Control Schemes

NITROGEN OXIDE EMISSIONS REDUCED FROM CEMENT KILN EXHAUST GASES
BY PROCESS MODIFICATION

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ABSTRACT

In January 1982 the South Coast Air Quality Management District (SCAQMD), El Monte, California, adopted a rule to reduce emissions of nitrogen oxides (NO_x) from the exhaust gases of portland cement kilns in the South Coast Air Basin. The rule was drafted to allow the cement manufacturers to demonstrate through research whether or not NO_x could be reduced by modification of the cement manufacturing process.

Riverside Cement Company, as a results of review of the literature and pilot studies conducted by KVB, Inc., selected the following four tactics as having potential for reducing NO_x emissions. These are: (1) reduce the quantity of fuel used per ton of clinker; (2) reduce the quantity and temperature of the primary air; (3) control of the configuration of the flame and (4) improve control of the operation of the kiln.

The Riverside Cement Company was able to demonstrate with statistical confidence that the NO_x emissions, after the implementation of the four tactics for the cement manufacturing process, were 26 percent less than the pre-modification emissions.

INTRODUCTION

Until the mid-1970's, nitrogen oxide (NO_x) emissions from cement kilns had received little attention in the United States, except for some plants that correlated NO_x emissions with burning-zone conditions to control the quality of the product (1). As research and regulations began to get a grasp upon the emissions of NO_x from electric power generating facilities and industrial boilers, interest in the control of NO_x emissions turned to the cement manufacturing industry.

In January 1982, the South Coast Air Quality Management District (SCAQMD) of California, USA adopted a rule which had a goal of reducing emissions of NO_x from portland cement kilns by 40 percent. The rule was drafted in such a way as to allow the cement manufacturers in the South Coast Air Basin to demonstrate through research whether or not a 40 percent reduction is feasible with reasonably available technology.

In response to this rule, Riverside Cement Company undertook an extensive program of research, engineering, plant redesign and monitoring at its Crestmore plant. This included a review of the literature, inspection of portland cement plants in Canada, Japan and the United States engaged in NO_x emissions research, participation in a Portland Cement Association investigation of the contribution of nitrogen in raw material to NO_x emissions, and participation in KVB pilot kiln studies on NO_x emissions. As a result, Riverside Cement Company concluded that the quantity of NO_x in the exit gases of a cement kiln may be lessened if the consumption of fuel is reduced and the control of the configuration of the flame is improved. These conclusions were drawn from the information in the literature about the affects of flame configuration on burning zone temperature (2), the laboratory evidence that burning zone temperature is related to NO_x emissions (3) and that NO_x emissions in kiln exit gases may be related to burning zone temperature (4 and 5). As a result of additional analysis from the data obtained from this study (6), there is a high positive correlation between burning zone temperature and NO_x emissions. These conclusions were supported by the evidence from an investigation of combustion modification technology (7).

As a result of the data available for NO_x emissions from the pre-modified system, it was concluded that the control (pre-modified) average emissions were 7.8 pounds of NO_x per ton of clinker (8). The experimental (post-modification) average emissions were 5.8. There was a 26 percent reduction in NO_x emissions of the experimental from the control system.

MATERIALS AND METHODS

MATERIALS

In early 1983, following extensive research, Riverside Cement Company began the modifications to its Crestmore Plant. These modifications made to the kiln and auxiliary equipment were based on the four tactics selected as the most likely to result in the reduction of fuel consumption and improved flame-configuration control.

MODIFICATIONS TO REDUCE FUEL USAGE

A redesigned kiln chain system was installed to reduce the quantity of fuel used. This system, composed of approximately 100 tons of a stainless steel curtain of chain, hung in a helical pattern, is alternately exposed to the 1600°F kiln gases

and the 100°F raw materials. As the kiln rotates, the chains transmit heat from the gases to the raw materials thereby conserving energy and reducing fuel usage.

The cooler throat of a kiln provides heated secondary air for combustion. If the throat is undersized, ambient air, which would require heating, is drawn from around the firing hood. To reduce this occurrence, the cooler throat was enlarged.

MODIFICATION TO REDUCE QUANTITY OF THE PRIMARY AIR

The direct firing system was converted to an indirect coal firing system in order to reduce the quantity of cool (175°F) primary air and replace it with hotter (1500°F) secondary air. In addition to reducing primary air from 34 to 15 percent of the total combustion air, the indirect system also vents the evaporated coal moisture to the atmosphere rather than to the kiln.

MODIFICATION TO PERMIT CONTROL OF THE FLAME CONFIGURATION

It has long been recognized that design factors of the burner pipe have a decided influence on flame control and kiln operations. It has also been recognized that the primary air velocity at the burner pipe and the ability to produce turbulent air flow are factors in flame control. Thus a specially designed burner was installed.

MODIFICATIONS TO ACHIEVE BETTER OPERATIONAL CONTROL OF THE KILN

Loss of flame control generally leads to cessation of the sintering reaction which produces the "clinker", the precursor of cement. To re-establish sintering requires increasing the flame temperature resulting in overheating of the kiln and additional NO_x formation. In addition to the increase of the cross-section of the cooler throat^x which resulted in a reduction of the velocity of air from the cooler, the clinker cooler fans, cooler dust collector, induction draft fan and kiln dust collector were renovated to provide better control of the air which would result in better flame control. The kiln instrumentation and the information from these instruments were improved so that the operator could be better informed about the operational conditions of the kiln.

METHOD

A Lear-Siegler (LSI) SM-810 NO_x/SO₂ gas analyzer, LSI CM-50 oxygen analyzer, Kaye Digilink, and IBM-PC were added to^x the existing instrumentation resulting in the collection of continuously monitored data from 45 field sensors. This continuously monitored data was averaged over six-minute intervals. KVB performed a quality assurance audit and in August of 1985 a dynamic calibration was performed on the NO_x and oxygen analyzers (9). Seven thousand sets of data were collected after this calibration was performed.

To insure that the measured NO_x emission rate reflects emissions during normal operating conditions, data was excluded when:

1. the kiln speed was less than 20 rph (indicating kiln start-up or shut-down);
2. MMBTU/ton was less than 3.5 or the coal feed rate was less than 2.0 tons per hour;
3. instruments were being calibrated and

4. the water spray was less than 20 gallons or greater than 70 gallons per minute (quantities outside of this range indicate malfunction of either the water spray or the water spray meter).

Data collected during temperature excursions were not excluded since these data are from normal operations.

The equation used to calculate pounds of NO_x per ton of clinker is:

$$\frac{\text{lb NO}_x}{\text{ton clinker}} = \frac{(\text{ppm NO}_x) (46) (1.56 \times 10^{-7}) (\text{SWCFM})}{\text{tons/hour clinker}} \quad (1)$$

where:

ppm NO_x = the measured volumetric concentration of NO (wet) of exhaust gases in parts per million.

tons/hour clinker = the production rate of the kiln.

SWCFM = the standard wet cubic feet per minute of exhaust gases.

Statistical parameters determined from the data were central tendency (average), dispersion (variance), standard deviation, standard error of the mean and sample size required to ensure the precision of the estimated mean to be no more than plus or minus 10 percent of the population mean. All methods and equations for the statistical evaluation were from Snedecor and Cochran (1980). The estimation of average pounds of NO_x per ton of clinker (central tendency) was made as a weighted average rather than an arithmetic average since an arithmetic average is not as accurate an estimate unless the production rate is constant. The equation for this estimation is:

$$\text{Weighted mean} = \bar{X} = \frac{\sum_{i=1}^n (Y_i) (P_i)}{\sum_{i=1}^n P_i} \quad (2)$$

where,

Y_i = NO_x observation in pounds per ton.

P_i = tons of production associated with Y emissions.

n = number of observations composing the weighted mean $\bar{X}$.

The hypotheses for testing the result of these modifications on the emissions of NO_x , stated statistically, is:

H_0 Post redesign and modification NO_x emissions are equal to pre-modification emissions; and

H_a Post redesign and modification NO_x emissions are less than pre-modification emissions (one tailed test).

Observation of variables pertaining to NO_x emissions began in August 1984 and continued through October 22, 1985. From these observations, six-minute averages were calculated. Daily, weighted mean emission rates were calculated from these six-minute averages. From the daily means statistical parameters were calculated.

The observations since August 1984 have been divided into three sets of data representing improvements in accuracy of the observations due to refinement of the monitoring system, improvements in calibration and development of a quality assurance/quality control program. The time periods of these sets of data are August 1984 through May 31, 1985, June 1, 1985 through August 13, 1985 and August 14, 1985 through October 22, 1985.

RESULTS

The kiln system was redesigned and modified in order to reduce the consumption of fuel and improve the control of the configuration of the flame. The tactics to accomplish these goals were conversion of the direct coal-fired system to an indirect coal-fired system, increase the cooler throat cross-section, renovate the gas handling system and install a new burner. The fuel consumption before these modifications was 5.0 MMBTU per ton of clinker and after the modifications was 4.5 MMBTU. The primary air volume was 34 percent of the total combustion air before the modifications and 15 percent after the modifications. As a result of the increase in the cross-section of the cooler throat, the velocity of the gases were reduced. The engineering goals of the project were accomplished.

From the daily means of each set of data, statistical parameters were calculated. The means for these sets of data are 6.1, 6.0 and 5.8 pounds of NO_x per ton of clinker (Table I). Although all of the data from August 1984 is available, and may be obtained upon request, the remaining presentation of statistical parameters is from the observations from the period August 14 through October 22, 1985. The 95 percent confidence interval about the mean of 5.8 (n=55) is 5.2 to 6.3, i.e., five percent of the population of means about the value 5.8 will fall outside of the range 5.2 to 6.3; all values within this range are considered not significantly different (probability = 0.05) from the value 5.8 pounds per ton. The average emission rates of the two earlier time periods are not significantly different (probability = 0.05) from the highly accurate emission rate of 5.8 pounds per ton.

There is no obvious trend in individual daily observations during the time period of August 14 to October 22 (Figure 1); the figure is one of random variation about a long-term mean. Variation between consecutive days ranges from less than 0.1 pound per ton to more than 7 pounds per ton, although changes between consecutive days are usually 1 to 2 pounds per ton.

Current daily average NO_x emissions appear to be normally distributed about the long-term mean of 5.8 pounds per ton (Figure 2) except for one unusually high observation of 14.3 pounds of NO_x per ton of clinker. This high observation occurred during a recovery from a temperature excursion, an undesirable operating condition when sintering takes place in a very short burning zone that is extremely hot. While temperature excursions are strenuously avoided since they cause severe kiln wear and damage, they occasionally occur on all kilns and are part of normal operation. NO_x emissions associated with temperature excursions generally lie outside of the range of expected normal variation.

The redesign and modification has resulted in a reduction from an average of 7.8 pounds per ton (pre-modification emissions rate) to the current rate of 5.8 pounds per ton. The 5.8 is significantly less than the 7.8 at the widely employed probability level in statistical inference of 0.05; in fact the expected distribution of repeated 55-day NO_x emission averages about the mean of 5.8 pounds per ton would include values of 7.8 or larger less than 1 in 10,000 times (probability less than 0.0001). Hence, the null hypothesis is rejected and the alternative hypothesis is accepted; the post-redesign and modification NO_x emission rate is significantly less than the pre-modification rate.

CONCLUSION

The results of this research indicates that the emissions of NO_x in the exit gas of a cement kiln can be reduced by reducing the amount of fuel consumption and control of the kiln operations, especially the configuration of the flame. However, it is quite obvious that this method of emissions reduction is limited to the level of NO_x emissions related to the most thermal efficient production of clinker. Beyond that level, further improvements in emissions reductions can come only from treatment of the exit gases. This is not to say that other system configurations, e.g., pre-heater, pre-calciner systems, cannot produce clinker at a lower level of NO_x emissions, but all systems will have a level at which emissions cannot be reduced further without affecting the quality of the clinker produced. At this level NO_x can, then, only be reduced by means other than add-on equipment to remove the NO_x from the exit gases.

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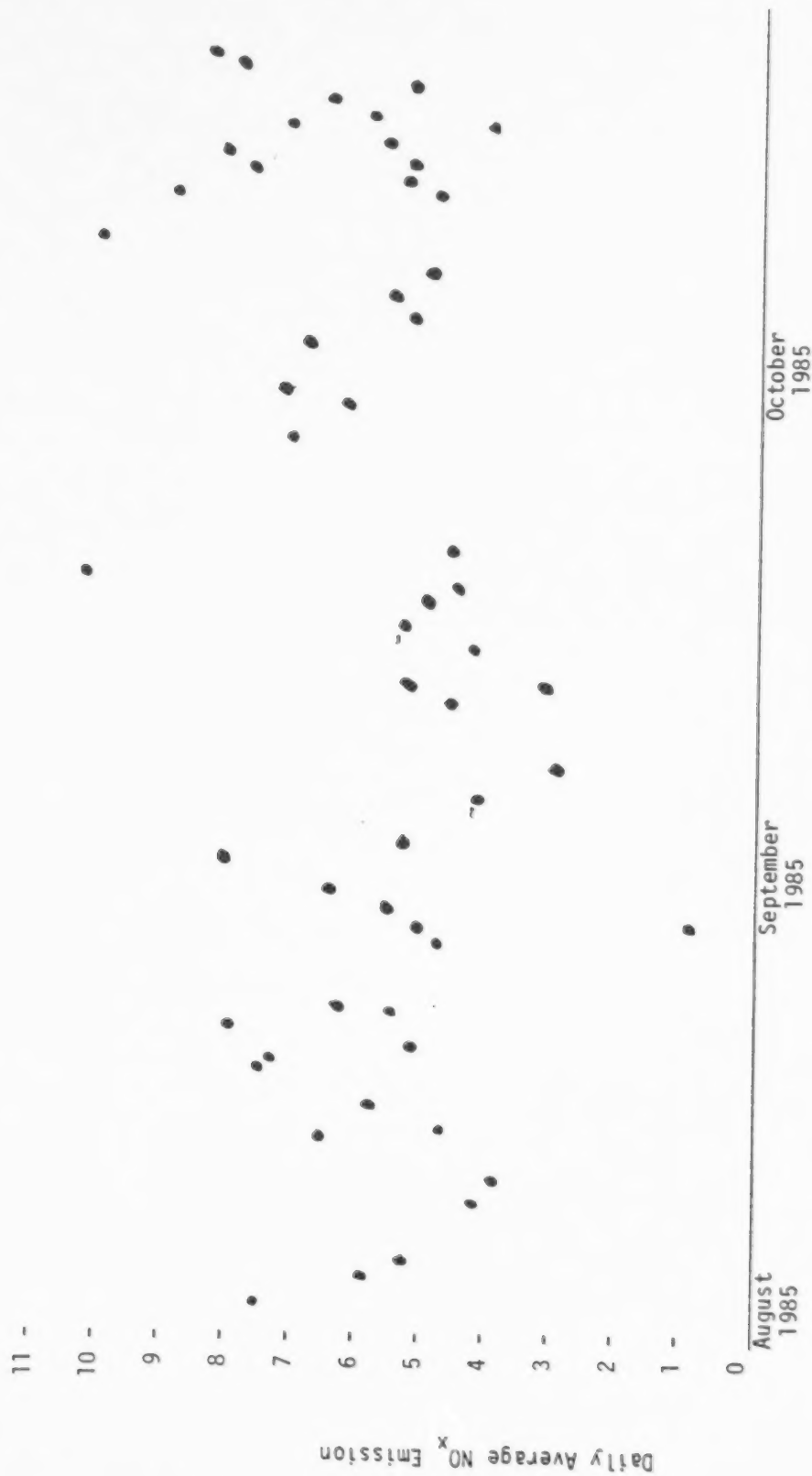


Figure 1. Daily Average NO_x Emissions: August 14, 1985 to October 22, 1985

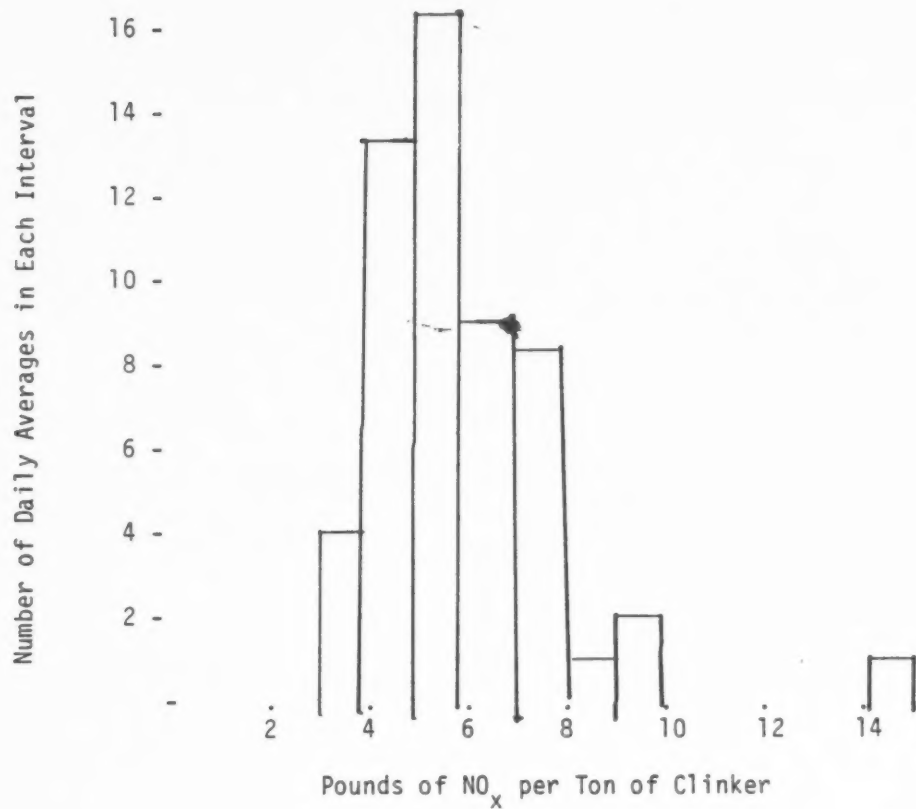


Figure 2. Frequency of Observations of Pounds of NO_x per Ton of Clinker (August 14, 1985 to October 22, 1985)

TABLE I. NO_x EMISSION RATES*

Time Period	Daily Mean	Standard Deviation	n
August 1984 - May 31, 1985	6.1	2.52	165
June 1 - August 13, 1985	6.0	2.21	64
August 14 - October 22, 1985	5.8	1.96	55

* Individual daily data may be obtained upon request from Professional Services and Management, 703 McKinney Avenue (Suite 302), Dallas, Texas 75202.

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ABSTRACT

NOx emissions from a cement kiln were analyzed with step-wise linear regression. The goal was to demonstrate which operating variable(s) control the rate of NOx emissions. Of 14 independent variables in the regression analysis, burning zone temperature of the kiln was the only significant variable; it accounted for 83% of the variability in NOx emissions. Because the burning zone required for production of acceptable quality clinker averages between 2400 - 2600 F, minimum NOx emission from a long, dry cement kiln is probably 5 - 6 pound of NOx per ton of clinker produced.

1.0 Introduction

We are presenting regression analysis of NO_x gases emitted from a long, dry cement kiln producing Type II clinker with indirect coal firing. Our presentation is the statistical analysis of data whose origin was described in the preceding paper prepared by May et al. Our purpose is to develop a statistical model, employing step-wise linear regression from pounds of NO_x per ton of clinker produced as the dependent variable; 47 other kiln operating variables were recorded simultaneously.

Nitrogen in NO_x from a cement kiln comes from process inputs (raw material and fuel) or from atmospheric nitrogen. Since feed and fuel nitrogen were essentially held constant (same source) during the 55 day period of operation during which our data were taken, variation in NO_x emissions most probably originate from combustion wherein atmospheric nitrogen is oxidized at high temperature to form NO_x, i.e. the formation of thermal NO_x.

Formation of oxides of nitrogen at high temperatures occurs in most combustion driven processes. A cement kiln offers the complexity of being an open ended, counter-current heat exchanger wherein there are, simultaneously, several endothermic and two or more exothermic reactions. Kiln regulation is best described as a fluctuating balance and its behavior as dynamic. Many variables regulate dynamic kiln operation. We will demonstrate which one or ones regulate thermal NO_x production.

2.0 Methods

2.1 Data

Data for this analysis were obtained during the period August 14 - October 22, 1985, during which the kiln operated all or portions of 55 days. NO_x in effluent gas was measured with a Lear-Siegler SM-810 NO_x/SO_x continuous gas analyser whose ppm signal was standardized to 3% oxygen. Other parameters relative to NO_x emissions were either measured (e.g. raw material) or calculated; details on data development can be found in Young, Mac Mann and Croom (1986). The datum point is a 6-minute average for each of 48 variables; 6984 data points were available for analysis.

2.2 Statistical Methods

Normal statistics were employed throughout and all predicted models are linear in their parameters. Statistical programs employed are supported by Burroughs under the title INFOSTATS/STATISTICS (1978); the specific regression program employed was STEPWISE. Probability to enter a variable into the model was arbitrarily set at 0.05. A variable was considered significant only if it accounted for at least 5% of the total sum of squares of the regression analysis.

2.3 Variable Selection

The step-wise regression program was capable of handling a maximum of 25 variables; therefore the list of 48 variables had to be winnowed to 25 or less with

NOx (lb/T) as the dependent variable. Winnowing was accomplished through three steps after cross correlating all 48 variables: 1) exclusion of those variables having a correlation coefficient with significance of less than 0.999; 2) exclusion of variables that may closely correlate with NOx but cannot actually affect NOx production, e.g. gas cooling water spray; 3) exclusion of one or more variables from a group measuring essentially the same process, i.e. a group of variables with exceedingly high cross-correlation, e.g. primary air percentage and primary air SCFM.

3.0 Results and Discussion

3.1 Range of Observations

Cement kilns operate under conditions where steady state is a goal and dynamic steady state is the result. During the 55 days of observation, 6 minute average NOx emissions ranged from approximately 0.5 lb/T to 18.1 lb/T; daily averages ranged from approximately 1 lb/T to 14.3 lb/T. As in all dynamic systems, the range of averages decreases as averaging time increases.

3.2 Variable Intercorrelation

Many of the 47 independent variables exhibited high correlation with NOx as they measured essentially the same parameter relative to NOx production e.g. temperature. Also, there were subsets of variables that exhibited extremely high intercorrelation as again they measured essentially the same parameter or process, e.g. kiln drive variables, clinker cooler variables. For mathematical consideration, it is essential to avoid, as much as possible, highly intercorrelated independent variables.

3.3 Variable Selection

Applying the winnowing criteria to the 47 independent variables resulted in selection of 14 independent variables to be included in step-wise regression (Table 1). Of the fourteen independent variables selected, nine relate to air flow; two involve clinker cooler operation; and the other three are clinker production, kiln revolutions per hour and burning zone temperature.

3.4 Regression Analysis

Step-wise regression determined that NOx production in a cement kiln was regulated almost entirely by burning zone temperature (BZT); the correlation coefficient was 0.83 for the model

$$\text{NOx} = 0.0022 \text{ BZT.} \quad (\text{Eq.1})$$

No other variable contributed more than an additional 4% to the regression sum of squares, and therefore were not considered significant variables in the regression.

Since burning zone temperature accounts for most of the variation in NOx emissions, thermal NOx, rather than fuel or feed NOx, is probably the major source of NOx emissions from this cement kiln. Our regression analysis is simplistic in its assumption of linear effect of BZT on NOx emissions; but in reality it is substantiated. NOx emissions probably approach infinity at 4000 F, but within the

range of our observations (1750 - 3450 F), NOx emissions were only slightly curvilinear (Figure 1). Over this range, our model (Equation 1 above) predicts within 6% the mean NOx emission (5.69 lb/T) of our nearly 7000 data points:

$$NO_x = 0.0022 \text{ BZT}$$

$$NO_x = 0.0022 (2742)$$

$$NO_x = 6.03 \text{ lb/T}$$

4.0 Conclusion

Reduction in NOx emissions through process engineering changes such as were made to this kiln can reduce NOx only so far. Acceptable quality clinkering reaction requires certain burning zone temperatures. At a realistic average BZT for acceptable quality clinker of 2400-2600 F, predicted NOx emissions are 5.3 and 5.7 lb/T. Therefore 5 - 6 lbs. of NOx per ton of clinker produced in a long, dry cement kiln may be the minimum achievable rate of NOx emissions by process modification only. Further reduction will probably require add-on modifications.

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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Table 1

Variables Included in Step-wise Regression of a Model
of NOx Emissions from a Cement Kiln

Dependent Variable

Pounds of NOx per ton of clinker produced (lb/T)

Independent variables

Air Flow Variables

- 1) Primary air as % of total air
- 2) Induced draft fan speed (RPM)
- 3) Induced draft fan amperage
- 4) Oxygen concentration at kiln exit
- 5) Secondary air temperature
- 6) Primary air temperature
- 7) Primary swirl air pressure
- 8) Primary axial air pressure
- 9) Primary air (SCFM)

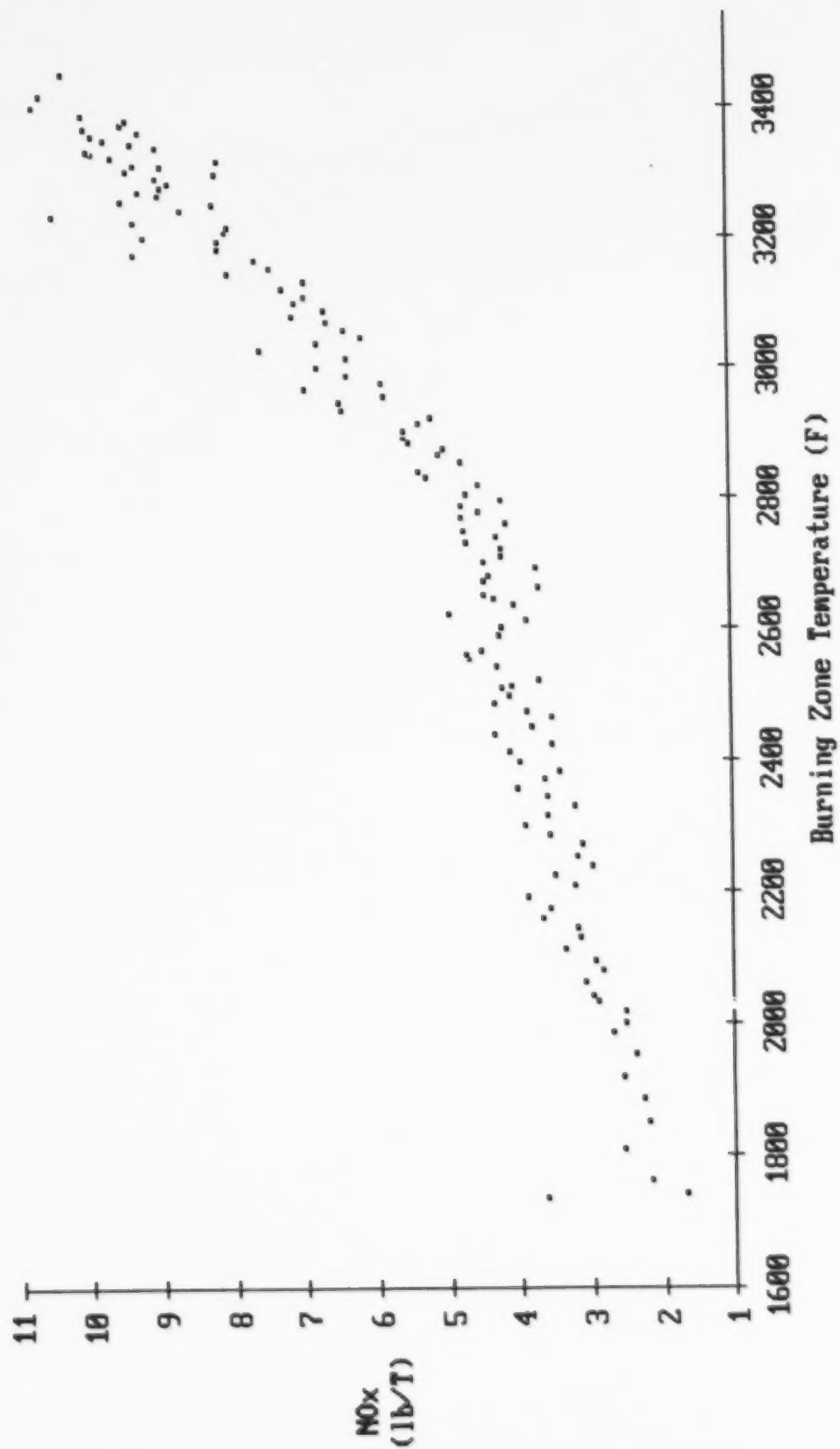
Clinker Cooler Variables

- 10) Lower grate undergrate pressure
- 11) Lower grate drive motor amperage

Other Variables

- 12) Production of clinker (T/hr)
- 13) Burning zone temperature (F)
- 14) Kiln rotational speed (RPH)

FIGURE 1
EIGHT HOUR AVERAGES OF NO_x FOR DATA SORTED BY BURNING ZONE
TEMPERATURE



Appendix A.

1987 Joint Symposium on Stationary Combustion NOx Control

03/23/87-03/26/87

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